

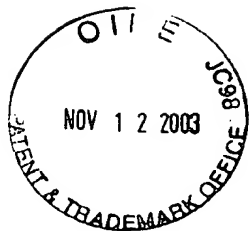
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DECLARATION

I, Junji Kamata, Patent Attorney, of SIKs & Co., 8th Floor, Kyobashi-Nisshoku Bldg., 8-7, Kyobashi 1-chome, Chuo-ku, Tokyo 104-0031 JAPAN hereby declare that I am the translator of the certified official copy of the documents in respect of an application for a patent filed in Japan on July 14, 2000 under Patent Application No. 213813/2000 and that the following is a true and correct translation to the best of my knowledge and belief.

Dated: November 5, 2003

Junji KAMATA



PATENT OFFICE

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This is to certify that the annexed is a true copy of the following application as filed with this office.

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Application Number : Patent Application No. 2000-213813
Applicant(s) : FUJI PHOTO FILM CO., LTD.

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【Document name】 Specification

【Title of the invention】 METHOD AND APPARATUS FOR PREPARING SILVER SALT OF ORGANIC ACID

【Claims】

【Claim 1】 A method for preparing a silver salt of an organic acid by reacting a silver ion solution as an aqueous solution containing silver ions and an organic acid alkali metal salt solution as a solution containing an alkali metal salt of an organic acid, in which the reaction is performed in sealed mixing means and which comprises steps of supplying the silver ion solution into a reaction field solution before introduced into the sealed mixing means, and supplying the organic acid alkali metal salt solution into the reaction field solution or sealed mixing means to which the silver ion solution has been supplied.

【Claim 2】 A method for preparing a silver salt of an organic acid according to Claim 1, wherein Reynolds number of the silver ion solution is in the range of 500–20000 when the silver ion solution is supplied to the reaction field solution.

【Claim 3】 A thermally processed image recording material using the silver salt of the organic acid obtained by the preparing method of claim 1 or 2.

【Claim 4】 An apparatus for preparing a silver salt of an organic acid, which comprises: a pipeline for supplying a silver ion solution as an aqueous solution containing silver ions; a pipeline for supplying an organic acid alkali metal salt solution as a solution containing an alkali metal salt of an organic acid; sealed mixing means; and a pipeline a pipeline for supplying a reaction field solution to the sealed mixing means, wherein the pipeline for supplying the silver ion solution is connected to the pipeline for supplying the reaction field solution, and the pipeline for supplying the organic acid alkali metal salt solution is connected to the sealed mixing means or the pipeline for supplying a reaction field solution at a position between a position at which the pipeline for supplying the silver ion solution is connected and the sealed mixing means.

【Claim 5】 An apparatus for preparing a silver salt of an organic acid, which comprises a pipeline for supplying a silver ion solution as an aqueous solution containing silver ions, a pipeline for supplying an organic acid alkali metal salt solution as a solution containing an alkali metal salt of an organic acid, first sealed mixing means, second sealed mixing means, a pipeline for connecting the first sealed mixing means and the second sealed mixing means and a pipeline for supplying a reaction field solution to the first sealed mixing means, wherein the pipeline for supplying the

silver ion solution is connected to the pipeline for supplying the reaction field solution to the first sealed mixing means or the first sealed mixing means, and the pipeline for supplying the organic acid alkali metal salt solution is connected to the pipeline for connecting the first sealed mixing means and the second sealed mixing means or the second sealed mixing means.

【Detailed description of the invention】

【0001】

【Filed of the invention】

The present invention relates to a method and an apparatus for preparing a silver salt of an organic acid. Particularly, the invention relates to a method and apparatus for preparing a silver salt of an organic acid to be used in a thermally processed image recording material and such a thermally processed image recording material using this silver salt of the organic acid.

【0002】

【Relevant art】

In recent years, reduction of amount of waste processing solutions has been strongly desired in the field of photographic-art process from the standpoints of environmental protection and space savings. Therefore, techniques relating to photothermographic materials for use in photographic-art processes and medical diagnosis are required to be developed, which enables efficient exposure by a laser image setter or laser imager and formation of a clear black image having high resolution and sharpness. Such photothermographic materials can provide users with a simpler and non-polluting heat development processing system that eliminates the use of solution-type processing chemicals.

【0003】

Methods for forming an image by heat development are described in, for example, U.S. Patent Nos. 3,152,904 and 3,457,075 and D. Klosterboer, "Thermally Processed Silver Systems", Imaging Processes and Materials, Neblette, 8th ed., compiled by J.Sturge, V. Walworth and A. Shepp, Chapter 9, p.279, (1989).

【0004】

Such thermally developing image recording material contains a reducible non-photosensitive silver source (e.g., organic acid silver salt), a photocatalyst (e.g., silver halide) in a catalytically active amount, and a silver reducing agent, which are usually dispersed in an organic binder matrix. The image recording material is stable at normal temperatures. When the material is heated at a high temperature (e.g.,

80°C or higher) after light exposure, silver is produced through an oxidation-reduction reaction between the reducible silver source (which functions as an oxidizing agent) and the reducing agent. The oxidation-reduction reaction is accelerated by catalytic action of a latent image generated upon exposure. Therefore, the silver which is produced by the reaction of the reducible silver salt in the light-exposed area becomes black, which forms an image in contrast to the non-exposed area.

【0005】

The silver source used in these systems is generally a silver salt of an organic acid, and various methods for producing it have been known. For example, there can be mentioned the method of preparing a silver salt of an organic acid in a solution under coexistence of water and a hardly water-soluble solvent as disclosed in Japanese Patent Laid-open Publication (Kokai, hereinafter referred to as JP-A) 49-93310, JP-A-49-94619, JP-A-53-68702, etc., the method of preparing a silver salt of an organic acid in an aqueous solution as disclosed in JP-A-53-31611, JP-A-54-4117, JP-A-54-46709, etc., the method of preparing a silver salt of an organic acid in an organic solvent as disclosed in JP-A-57-186745, JP-A-47-9432, U.S. Patent No. 3,700,458 and so forth. Basically, the preparation is carried out by heating an organic acid to a temperature higher than its melting point to melt it in water, adding sodium hydroxide or an alkali metal salt with vigorous stirring to make an alkali metal salt of the organic acid, and then adding silver nitrate in order to convert the alkali metal salt of the organic acid into a silver salt of the organic acid.

【0006】

The alkali metal salt of the organic acid forms micelles in an aqueous solution, and gives a solution of whitely turbid appearance. The reaction from the alkali metal salt of the organic acid in such a micelle state to the silver salt thereof often suffers from problems concerning production stability. Therefore, as a method for obtaining the alkali metal salt of the organic acid as a uniform solution, a method of using a mixed solution of water and alcohol as the solvent is disclosed in JP-A-55-40607.

【0007】

Further, since the alkali metal salt of the organic acid presents alkalinity as its name shows, the silver salt of the organic acid will be prepared under a high pH condition in the above conversion reaction. However, addition of silver nitrate into the alkaline solution produces silver oxide as a by-product. Further, it also

generates unintended silver nuclei produced by a trace amount of reducing contaminants, which are unavoidably mixed into the reaction solution in view of production process and exhibit high reducing property due to the high pH. Such by-products are extremely disadvantageous from the viewpoint that they degrade performance of photothermographic materials, in particular, they cause undesired fog. In this respect, the problem of the fog is not solved even in the method disclosed in JP-A-55-40607, which aims at obtaining a uniform solution in order to suppress the generation of the by-products.

【0008】

Further, JP-A-9-127643 discloses a method for producing a silver salt by simultaneous addition of measured amounts of an alkali metal salt solution and a silver nitrate solution, and refers to simultaneous addition of a solution of sodium behenate in a mixture of water and isopropyl alcohol and a solution of silver nitrate. This method can at least shift the pH of the reaction from the high pH region to a neutral region, and thus it is a preferred method for reducing the generation amount of silver oxide. However, isopropyl alcohol shows weak reducing property, and this makes the method insufficient as a method for completely solving the problem of fog.

【0009】

As mentioned above, it is necessary to pay attention to the preparation of the silver salts of the organic acids. During the formation of the silver salt of the organic acid, it is necessary to omit the reducible material as much as possible, control the size of the grains, and further control the shapes of the grains. However, these are not realized by the conventional methods.

【0010】

As to the thermally processed image recording materials using the heretofore known silver salts of the organic acids, image forming layers are formed in many cases by applying coating liquids with organic solvents such as toluene, methyl ethyl ketone, methanol, etc. as solvents. Use of the organic solvents as solvents not only causes adverse influences upon human bodies during the producing process, but also requires other steps such as recovery of the solvents. Thus, it is extremely disadvantageous in view of the cost performance. It can be said that there is no suitable producing method as providing the thermally processed image recording materials aiming at the environmental protection.

【0011】

Under the circumstances, there are proposed methods of forming image forming layers by using coating liquids with water as a solvent. For example, image forming layers using gelatin as a binder are described in JP-A-49-52626, JP-A-53-116144, etc. Further, an image forming layer using a polyvinyl alcohol as a binder is described in JP-A-50-151138. Furthermore, an image forming layer using gelatin and polyvinyl alcohol in combination is described in JP-A-60-61747. An image forming layer using a water-soluble polyvinyl acetal as a binder is described in JP-A-58-28737.

【0012】

When such water-soluble polymers are used as binders, image forming layers can be formed by using coating liquids with water solvent, so that there are great merits in environment and cost. However, If coating liquid containing the above-mentioned water-soluble polymer binder and the silver salt of the organic acid is used, there are problems that the quality of the coated face cannot withstand practical use, that the hue of silver images in developed areas becomes brown or yellow largely different from black essentially preferred, and that fog is much. Thus, such image forming layers could provide merely conspicuously deteriorated commercial product values.

【0013】

In order to obtain the practically employable quality of a coated face by using a water solvent coating solution containing a silver salt of an organic acid, it is necessary to attain a state that the silver salt of an organic acid is finely dispersed in the water solvent without aggregation. For this reason, it is necessary to develop a method for dispersing the silver salt of an organic acid as fine grains. Usually used is a method comprising separating the formed hydrophobic grains of silver salt of an organic acid as solid by filtration, mixing a dispersing agent with the solid, and dispersing the mixture again, as described in "Thermally processed Silver System", Imaging Processes and Materials, Neblette, 8th ed., compiled by J.Sturge, V. Walworth and A. Shepp, Chapter 9, p.279, (1989), for example.

【0014】

As the method for dispersing a silver salt of an organic acid as fine grains, the method of mechanically dispersing it in the presence of a dispersing aid by means of known pulverization mean (e.g., high-speed mixer, homogenizer, high-speed impact mill, Banbary mixer, homomixer, kneader, ball mill, vibrating ball mill, planetary

ball mill, attriter, sand mill, bead mill, colloid mill, jet mill, roller mill, trone mill and high-speed stone mill). However, this method not only produces only a coating solution containing a lot of aggregated particles, i.e., a coating solution that gives bad coated surface quality, but also suffers from a problem that, because the method highly possibly grinds primary grains of a silver salt of an organic salt crystallized as a hardly water-soluble salt without any selectivity, silver nuclei are formed at crystal cleavage surfaces and causes increase of fog.

【0015】

Although a method of finely dispersing silver salt of fatty acids under pressurizing is described in JP-B-119953, JP-A-8-137044 and JP-A-238848, they relate to dispersed products with organic solvents as solvents. They differ in character from the solving of the above problems.

【0016】

Further, JP-A-9-127643 discloses a method of directly desalting a dispersion of a silver salt of a fatty acid obtained by simultaneous addition of measured amounts of a solution of an alkali metal salt and a silver nitrate solution by means of dialysis or ultrafiltration. This method is preferred in that at least the primary grains obtained during the crystallization of the silver salt of the fatty acid can be introduced into a image forming layer without degrading the primary grains. However, problems concerning aggregation of grains under a high salt concentration circumstance, increase of viscosity upon concentration of the dispersion and so forth are not solved, and thus this method is still insufficient as practical means for obtaining a uniform dispersion.

【0017】

In order to obtain monodispersed grains of a silver salt of an organic acid as fine grains, vigorous stirring is required during the addition of an alkali metal salt solution of the organic acid and a solution of silver nitrate. In particular, the solution of an organic acid alkali metal salt dissolved at a high temperature suffers from temperature decrease and shows precipitation upon addition thereof, and therefore large grains may grow if dilution rate or fluidization is slow or weak. Alternatively, coarse grains of the organic acid alkali metal salt may precipitate without the organic acid silver salt being obtained. In order to carry out a more homogeneous reaction, the concentration of each of the starting materials needs to be rapidly made uniform. However, a flow rate is small in pipelines or along a wall of a mixer where the liquids added move slowly. Consequently, even if stirring is

more vigorously effected by the mixer, there occur portions where rapid mixing is not made as intended.

【0018】

Further, when they are added to a tank in which a gas/liquid interface is present, and the stirring speed is increased, entrainment of air is caused. The grains of silver salt of the organic acid are highly hydrophobic, and therefore not only the grains are adsorbed on the surfaces of the entrained bubbles to stabilize the bubbles and prevent breakage of them, but also the adjacent grains on the bubbles cause aggregation. The liquid containing air entrained in such a manner becomes a whipped cream-like liquid. When a byproduct salt is to be removed from the liquid by ultrafiltration or the like, handling facility is extremely deteriorated, and aggregated grains cause clogging.

【0019】

As described above, any stable method has not been found yet, in which a water solvent coating liquid is obtained to provide a thermally processed image recording material having a good coated surface quality with excellent optical performance as to such as haze and fog.

【0020】

【Problems to be resolved by the invention】

Therefore, the problem to be solved by the present invention is to provide a method for preparing a silver salt of an organic acid, which gives a photothermographic material having high sensitivity and high image stability after thermal processing when the silver salt is used for the photothermographic material.

【0021】

【Means which Solve the Problems】

The present inventors repeatedly made strenuous investigations, and consequently found out that the problem can be solved by a method for preparing a silver salt of an organic acid according to the present invention. That is, the present invention relates a method for preparing a silver salt of an organic acid by reacting a silver ion solution as an aqueous solution containing silver ions and an organic acid alkali metal salt solution as a solution containing the alkali metal salt of the organic acid, in which the reaction is performed in sealed mixing means and which comprises steps of supplying the solution containing silver ions into a reaction field solution before introduced into the sealed mixing means, and supplying the solution containing an alkali metal salt of an organic acid into the reaction field solution or sealed mixing

means to which the solution containing silver ions has been supplied. According to the invention method for preparing the organic acid silver salt, the Reynolds number of the solution containing silver ions is preferably in the range of 500–20000 when the solution containing silver ions is supplied to the reaction field solution. In the present specification, “–” in “500–20000” includes the figures given before and after that as a minimum value and a maximum value, respectively. The present invention also provide thermally processed image recording material using the organic acid silver salt obtained by the above preparing method.

【0022】

The present invention also provides an apparatus for preparing a silver salt of an organic acid, which comprises a pipeline for supplying a silver ion solution as an aqueous solution containing silver ions, a pipeline for supplying an organic acid alkali metal salt solution as a solution containing an alkali metal salt of an organic acid, sealed mixing means and a pipeline for supplying a reaction field solution to the sealed mixing means, wherein the pipeline for supplying the silver ion solution is connected to the pipeline for supplying the reaction field solution, and the pipeline for supplying the organic acid alkali metal salt solution is connected to the sealed mixing means or the pipeline for supplying a reaction field solution at a position between a position at which the pipeline for supplying the silver ion solution is connected and the sealed mixing means. Further, the present invention also provides an apparatus for preparing a silver salt of an organic acid, which comprises a pipeline for supplying a silver ion solution as an aqueous solution containing silver ions, a pipeline for supplying an organic acid alkali metal salt solution as a solution containing an alkali metal salt of an organic acid, first sealed mixing means, second sealed mixing means, a pipeline for connecting the first sealed mixing means and the second sealed mixing means and a pipeline for supplying a reaction field solution to the first sealed mixing means, wherein the pipeline for supplying the silver ion solution is connected to the pipeline for supplying the reaction field solution to the first sealed mixing means or the first sealed mixing means, and the pipeline for supplying the organic acid alkali metal salt solution is connected to the pipeline for connecting the first sealed mixing means and the second sealed mixing means or the second sealed mixing means.

【0023】

【Embodiments of the Invention】

Hereafter, the methods for producing a silver salt of an organic acid, thermally processed image recording materials and an apparatus for preparing such

an organic acid silver salt of the present invention will be explained in detail. The present invention relates to a method for preparing a silver salt of an organic acid by reacting a silver ion solution and an organic acid alkali metal salt solution, in which the reaction is performed in sealed mixing means and which comprises steps of supplying the silver ion solution into a reaction field solution before introduced into the sealed mixing means, and supplying the solution containing the alkali metal salt of the organic acid into the reaction field solution or sealed mixing means.

【0024】

Figs. 1 and 2 show schematic views of a method for preparing a silver salt of an organic acid according to the present invention. In the figures, 1, 3 and 4 denote sealed and liquid-filled mixers. A, B and C denote pipelines for supplying a silver ion solution, an organic acid alkali metal salt solution and a reaction field solution, respectively. These liquids are stirred and reacted in the sealed mixers, and the resulting solution of the organic acid silver salt is taken out through a pipeline E.

【0025】

Fig. 3 shows an embodiment of the method for preparing the silver salt of the organic acid according to the present invention. In the figure, the silver ion solution and the organic acid alkali metal salt solution are stored in tanks 11 and 12, respectively, while their temperatures are set at their respectively given temperatures. Flow meters 13 and 14 measure respective flow rates of the these solutions when they are added to a sealed and liquid-filled mixer 18 via pumps 15 and 16, respectively. This embodiment is equipped with a pump 17 for supplying again a dispersion of the silver salt of the organic acid prepared as a third component to the mixer 18.

【0026】

Fig. 4 is an enlarged view of a mixing part in an organic acid silver salt-preparing method as a comparison. Figs. 5 to 7 are enlarged views of mixing parts in other embodiments of the organic acid silver salt-preparing method according to the present invention.

【0027】

The “organic acid” for the alkali metal salt of the organic acid used in the present invention is an organic acid which is relatively stable to light when it is converted to a silver salt and which produces a silver image when the silver salt is heated at 80°C or higher in the presence of a light exposed photocatalyst (e.g., latent

images of photosensitive silver halide) and a reducing agent. The organic acid is preferably a long chain aliphatic carboxylic acid which contains preferably 10–30 carbon atoms, more preferably 12–26 carbon atoms. Preferred examples of the aliphatic carboxylic acid include cerotic acid, lignoceric acid, behenic acid, erucic acid, arachidic acid, stearic acid, oleic acid, lauric acid, caproic acid, myristic acid, palmitic acid, maleic acid, fumaric acid, tartaric acid, linolic acid, butyric acid, camphoric acid and mixtures thereof.

【0028】

As the “alkali metal” for the alkali metal salt of an organic acid, sodium, potassium and so forth can be specifically mentioned. An alkali metal salt of an organic acid can be prepared by adding sodium hydroxide, potassium hydroxide or the like to an organic acid. In this treatment, it is preferable to use the alkali in an amount less than the equivalent of the organic acid to remain unreacted organic acid. In this case, the amount of the remaining organic acid is preferably 3–50 mole %, more preferably 3–30 mole %, with respect to the total organic acid. Further, it may be prepared by adding an alkali in an amount exceeding the desired amount, and then adding an acid such as nitric acid and sulfuric acid to neutralize excessive alkali substance. The alkali metal salt solution of the organic acid may be either a mixed solution of an organic solvent and water or a solution or suspension containing the organic acid alkali metal salt in the organic solvent.

【0029】

The “silver ion solution” used in the present invention has only to be a solution in which a water-soluble silver salt is dissolved. As the water-soluble silver salt, silver nitrate is preferred. The silver ion solution used in the present invention, which is an aqueous solution containing silver ions, preferably has a Reynolds number in the range of 500–20,000, when the solution containing silver ions is supplied.

【0030】

The “reaction field solution” used for the present invention consists of water or a mixed aqueous solution of water and an organic solvent. The reaction field solution may contain a dispersing agent, and it may be a recycled portion of the organic acid silver salt solution obtained in the reaction as shown in Fig. 3.

【0031】

In the present invention, the solution containing silver ions is supplied to the reaction field solution, and then the solution containing an alkali metal salt of an organic acid is supplied to the reaction field solution or the sealed mixing means.

When the solution containing an alkali metal salt of an organic acid is supplied to the reaction field solution before being supplied to the sealed mixing means, the organic acid alkali metal salt solution is supplied after the silver ion solution is supplied. That is, the silver ions need to be present at a point of time when the organic acid alkali metal salt solution is supplied to and mixed with the silver ion solution. If the amount of the silver ions present is small, the organic acid alkali metal salt itself is deposited as coarse grains.

【0032】

A distance between a silver ion solution-supplying position and an organic acid alkali metal salt solution-supplying position is preferably 2 to 20 times as large as the diameter of the reaction field solution pipeline to which both the solutions are supplied. When the organic acid alkali metal salt solution is supplied to the sealed mixing means, a distance between the silver ion solution-supplying position and the connection between the reaction field solution-supplying pipeline and the sealed mixing means is preferably 2 to 20 times as large as the diameter of the reaction field solution-supplying pipeline. In the present invention, two sealed mixing means can be provided. In this case, it may be that the silver ion solution is supplied to the first sealed mixing means or the reaction field solution-supplying pipeline upstream the first sealed mixing means, and the organic acid alkali metal salt solution is supplied to the second sealed mixing means downstream the first one or a pipeline connecting the first and second sealed mixing means. Another sealed mixing means may be provided downstream of the above sealed mixing means where the silver ion solution is reacted with the organic acid metal salt solution.

【0033】

The organic acid silver salt-preparing apparatus according to the present invention will be explained. A first embodiment of the organic acid silver salt-preparing apparatus of the invention comprises a pipeline for supplying a silver ion solution, a pipeline for supplying an organic acid alkali metal salt solution, sealed mixing means and a pipeline for supplying a reaction field solution to the sealed mixing means. The silver ion solution and the organic acid alkali metal salt solution are prepared in separate preparing tanks, respectively, and are supplied from their respective preparing tank through pipelines by ordinary discharge means such as pumps. Their supply amounts are adjusted by ordinary flowmeters, respectively. The pipeline for supplying the silver ion solution is connected to the pipeline for

supplying the reaction field solution, and the pipeline for supplying the organic acid alkali metal salt solution is connected to the sealed mixing means or the pipeline for supplying a reaction field solution at a position between the pipeline for supplying the silver ion solution and the sealed mixing means.

【0034】

A second embodiment of the organic acid silver salt-preparing apparatus according to the present invention comprises a pipeline for supplying a silver ion solution, a pipeline for supplying an organic acid alkali metal salt solution, first sealed mixing means, second sealed mixing means connected to a downstream side of the first sealed mixing means, and a pipeline for supplying a reaction field solution to the first sealed mixing means. The pipeline for supplying the silver ion solution is connected to the pipeline for supplying the reaction field solution to the first sealed mixing means or the first sealed mixing means, and the pipeline for supplying the organic acid alkali metal salt solution is connected to the pipeline for connecting the first sealed mixing means and the second sealed mixing means or the second sealed mixing means. The other construction is the same as in the first embodiment.

【0035】

The sealed mixing means used in the present invention is not limited so long as it is mixing-stirring means having no gas/liquid interface. The sealed mixing means may be any such means, and examples thereof include, for example, rotary stirrers and emulsification dispersion machines such as those provided with paddles and propellers, dissolvers and rotary homogenizers, static type mixers such as reciprocal motion type stirrers, static mixers and throughother mixers, combinations thereof and so forth. Although depending upon the diameter of the impeller, the velocity at the outermost periphery of the impeller (so-called peripheral velocity) is preferably 1-30 m/second, and more preferably 2-20 m/second. Although depending upon the size of the a vessel of the sealed mixing means and the flow rate of the solution, the volume of the vessel of the sealed mixing means is preferably one giving a retention time of 0.2-10 seconds, preferably 0.5-5 seconds. As the sealed mixing means, a commercial device may be used, and pipeline mixers, Model LR-1 and Model PM-20 produced by Mizuho Kogyo Co., Ltd., etc. may be recited.

【0036】

The pH of the solution containing silver ions is preferably 1-6, more preferably 1.4-4. For the pH adjustment, any acid or alkaline may be added to the solution

containing silver ions.

【0037】

The concentration of the silver salt in the silver ion solution used in the present invention, which is arbitrarily determined, is preferably 0.03–6.5 mol/L, more preferably 0.1–5 mol/L.

【0038】

According to the present invention, in order to produce organic acid silver salt grains, it is preferable to add an organic solvent to at least one of the solution containing silver ions, the solution containing organic acid alkali metal salt and the solution prepared in the reaction field beforehand in such an amount that the alkali metal salt of the organic acid can be present so as to form a substantially transparent solution without forming linear aggregates or micelles. The organic acid alkali metal salt solution and the reaction field solution may include an organic solvent alone, but a mixed solution between water is preferable.

【0039】

As the organic solvent used in the present invention, it is not particularly limited so long as it is miscible with water, provided that the organic acid alkali metal salt does not form the linear aggregates or micelles and the organic solvent does not degrade photographic performance. Preferred solvents are water-miscible alcohols and acetone, and a tertiary alcohol having 4–6 carbon atoms is more preferred.

【0040】

The solution containing silver ions, the solution containing an alkali metal salt of an organic acid and the reaction field solution used for the present invention may be added with compounds of the formula (1) described in JP-A-62-65035, water-soluble group-containing N-heterocyclic compounds such as those described in JP-A-62-150240, inorganic peroxides such as those described in JP-A-50-101019, sulfur compounds such as those described in JP-A-51-78319, disulfide compounds such as those described in JP-A-57-643, hydrogen peroxide and so forth.

【0041】

The solvent used for the solution containing the alkali metal salt of the organic acid used for the present invention may be a mixture of water and an organic solvent. In this case, the amount of the organic solvent is preferably 3–70 volume %, more preferably 5–50 volume %, with respect to the volume of water.

Since the optimum solvent volume varies depending on the reaction temperature, the optimum amount can be determined trial-and-error basis.

【0042】

The concentration of the alkali metal salt of the organic acid in the solution containing the alkali metal salt of the organic acid used for the present invention is preferably 5–50 weight %, more preferably 7–45 weight %, further preferably 10–40 weight %.

【0043】

The silver ion solution and the organic acid alkali metal salt solution used in the present invention can be used at appropriate temperatures. The temperature of the silver ion solution is preferably 5–60°C, preferably 5–40°C so as to ensure the stability of the solution. The temperature of the organic acid alkali metal salt solution is preferably 50–90°C, preferably 50–90°C so as to avoid crystallization and solidification of the alkali soap.

【0044】

In order to rapidly lower the liquid temperature of the reaction mixture after the reaction of the solution containing silver ions and the solution containing organic acid alkali metal salt, the solution containing silver ions, water or a mixed solution of water and an organic solvent or the solution containing the reacted organic acid silver salt to be supplied to the sealed mixing means may be cooled beforehand by means of a heat exchanger or the like. Further, cooling of the sealed mixture means itself or provision of a heat exchanger between the sealed mixing means and a tank can be employed. The liquid temperature after the reaction of the solution containing silver ions and the solution containing organic acid alkali metal salt is preferably 5–70° C, more preferably 10–50° C, particularly preferably 20–45° C. Further, as for the cooling rate, performance as a photosensitive material can further be improved, if the temperature reaches a desired temperature within 0.05–10 seconds, preferably 0.05–5 second, further preferably 0.05–1 second, after the reaction solutions are brought into contact with each other.

【0045】

The heat exchanger used for cooling is not particularly limited. For example, there can be used a multi-pipe cylinder type heat exchanger, heat pipe type heat exchanger, double pipe type heat exchanger, coiled type heat exchanger, cascade type heat exchanger, plate type heat exchanger, spiral plate type heat

exchanger, water-cooled heat exchanger and so forth.

【0046】

The organic acid silver salt grains prepared in the present invention preferably have a diameter as sphere of 0.1–0.8 μm , more preferably 0.1–0.6 μm . Further, they preferably have a ratio of long side length/short side length of grains of 1–4, more preferably 1–3, particularly preferably 1–2. Furthermore, the grains preferably have an aspect ratio (grain size for main plane (diameter as circle)/thickness of grain) of 2–30, more preferably 2–15. Further, the grains preferably have a thickness of is 0.01–0.20 μm , more preferably 0.01–0.15 μm . The grains are characterized by containing such grains satisfying the aforementioned requirements in an amount of 30–100%, more preferably 50–100%, particularly preferably 70–100%, in terms of a ratio to the projected area of total grains.

【0047】

The grain size distribution of the silver salt of an organic acid is preferably monodispersed one as far as possible. When a coefficient of variation is defined as a value 100 times as large as a value obtained by dividing the standard deviation of grain size by the grain size, the coefficient of variation is preferably 20% or less, more preferably 18% or less, further preferably 15% or less. As for the measurement method, for example, the grain size (volume weight average diameter) can be determined by irradiating silver salt of an organic acid dispersed in a liquid with a laser ray and determining an autocorrelation function of the fluctuation of the scattered light on the basis of the change in time (the so-called dynamic light scattering method).

【0048】

A water-soluble dispersant may be added to the silver ion solution, the organic acid alkali metal salt solution and the reaction field solution. Therefore, the dispersant can be contained in the reaction solution at the time of and after the formation of the organic acid silver salt. Any dispersant is acceptable so long as it can disperse the formed organic acid silver salt. Specific examples of the dispersant are those for the organic acid silver salts as mentioned later.

【0049】

As to the shape of the organic acid silver salt obtained by the present invention, scaly grains are preferred. Grains generally known as grains of behenic acid, for example, acicular grains having minor and major axes as described in Handbook of Imaging Materials compiled by A. S. Diamond, p 45, Fig. 2.2, Marcel

Dekker (1991) or grains having no selectively growing direction as described in JP-A-9-127643 are not preferable.

【0050】

The present invention preferably employs a method of forming a dispersion of fine solid grains by using a dispersant so as to obtain fine grains of the aggregation-free organic acid silver salt having small grain sizes. The grains of the organic acid silver salt are preferably washed with water prior to making the dispersion. It is preferable that only the aggregation is diminished in forming the dispersion of the fine solid grains without breaking the formed grains. Such a state can be judged by comparing TEM photographs of the grains of the organic acid silver salt before washing with water and those after washing and dispersion. In the present invention, it is preferable that the projected area does not change by preferably not less than 30%, more preferably not less than 20%, further preferably not less than 10% when the average grain size before washing is compared with that after washing. The above washing is not limited to a particular method. For example, a method of filtering the solid by suction filtration or the like and then washing it with distilled water can be employed. As to the dispersing method, it is preferable to convert the aqueous dispersion of the organic acid silver salt to a high pressure/high speed flow and decrease the pressure.

【0051】

When a photosensitive silver salt coexists at the time of dispersing process, fog may increase and sensitivity may markedly decrease. Therefore, the dispersion during the dispersing process preferably contains substantially no photosensitive silver salt. In the present invention, the amount of photosensitive silver salt in the aqueous dispersion is desirably 0.1 mole % or less per 1 mole of silver salt of the organic acid silver salt in the dispersion, and it is desirable not to intentionally add photosensitive silver halide salt.

【0052】

The dispersing machines and techniques used for performing the above-described dispersion method are described in detail, for example, in Toshio Kajiuchi and Hiromoto Usui, *Bunsan-kei Rheology to Bunsanka Gijutsu (Rheology of Dispersion System and Dispersion Technology)*, pp.357-403, Shinzan Sha Shuppan (1991), and *Kagaku Kogaku no Shinpo (Progress of Chemical Engineering)*, vol. 24, pp. 184-185, compiled by Corporation Kagaku Kogakukai Tokai Shibu, Maki Shoten (1990), and so forth. The dispersion method used in the present invention comprises at

least the steps of supplying an aqueous dispersion containing the silver salt of the organic acid into a pipeline under a positive pressure by means of a high-pressure pump or the like, passing the dispersion through a narrow slit provided inside the pipeline, and then subjecting the dispersion to rapid pressure release to perform fine dispersion.

【0053】

As for the high-pressure homogenizer with which the present invention is concerned, it is generally considered that fine dispersion can be achieved therein by dispersing forces such as "shear force" generated at the passage of a dispersoid through a narrow slit under high pressure at high speed and "cavitation force" generated when the dispersoid is released from the high pressure to ordinary pressure. An example of the dispersion apparatus of this type is a Golline homogenizer. In this apparatus, a liquid to be dispersed, which is introduced under high pressure, is converted into a high-speed flow when it is passed through a narrow gap formed on the wall of a cylindrical surface. Then, the flow collides against a surrounding wall with its own force, and is emulsified and dispersed by the impact force. The pressure to be use is generally 100 to 600 kg/cm², and the flow rate is generally a few meters/sec to 30 meters/sec. In order to increase the dispersion efficiency, some apparatuses are designed wherein the high flow rate area is so modified as to have a serrated configuration, thereby increasing the frequency of collision. Typical examples of such apparatuses are Microfluidizer produced by Microfluidex International Corporation, Nanomizer from Tokushu Kika Kogyo Co., Ltd, etc.

【0054】

In the present invention, the organic acid silver salt can be dispersed in a desired grain size by adjusting the flow rate, the differential pressure at the time of the pressure decrease and the number of times of the treatment. It is preferable from the photographic performance and the grain size that the flow rate is in a range of 200–600 m/second, and the differential pressure at the time of the pressure decrease is in a range of 900–3000 kg/cm². More preferably, the flow rate is in a range of 300–600 m/second, and the differential pressure at the time of the pressure decrease is in a range of 1500–3000 kg/cm². The number of times of the dispersing treatment can be selected according to the need. It is usually in a range of 1–10 times, and around 1–3 times is selected from the standpoint of the productivity. It is not preferable to expose such an aqueous dispersion to a high

temperature under a high pressure in view of dispersibility and photographic performance. At a high temperature above 90°C, a grain size may readily become large and fog may be increased. Therefore, according to the present invention, a cooling apparatus is preferably provided before a step where the solution is converted to the high pressure and high-speed flow as mentioned above, or a step after the pressure decrease or in both the steps. Accordingly, the water dispersion is preferably kept at a temperature of from 5°C to 90°C, more preferably from 5°C to 80°C, particularly preferably from 5°C to 65°C, by the cooling step. In particular, when the dispersion is made at high pressure in a range of 150 to 3000 kg/cm², the above cooling step is effectively provided. The cooling apparatus may be appropriately selected from a multi-tubular heat exchanger, a double pipe or triple pipe which may be combined with a static mixer, a plate type heat exchanger, a swirl plate type heat exchanger and so forth, depending on an amount of heat exchange to be required. The size, wall thickness or material of pipes may be appropriately selected to increase heat exchange efficiency depending on an applied pressure. In addition, depending on an amount of heat exchange, a refrigerant used in the cooling apparatus may be a well water at 20°C or a chilled water at from 5 to 10°C cooled by a refrigerator, and if desired, a refrigerant such as ethylene glycol/water at -30°C may also be used.

【0055】

The dispersing agent can suitably be selected for use from known polymers, for example, synthetic anionic polymers such as polyacrylic acid copolymers, maleic acid copolymers, maleic acid monoester copolymers, acryloylmethylpropane-sulfonic acid copolymers, etc.; semi-synthetic anionic polymers such as carboxymethyl starch and carboxymethyl cellulose; anionic polymers of such as alginic acid and pectic acid; anionic surface active agents described in JP-A-52-92716, International Publication WO88/04794 and so forth, compounds described in JP-A-7-350753, publicly known anionic, publicly known nonionic and cationic surface active agents, publicly known polymers such as polyvinyl alcohol, polyvinylpyrrolidone, carboxymethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose etc., naturally occurring macromolecular compounds such as gelatin and so forth. The concentration of the dispersing agent is preferably 1-30 weight%, more preferably 3-20 weight% relative to the organic acid silver salt.

【0056】

The prepared dispersion can be stored with stirring to prevent precipitation of the grains during storage, or stored in a highly viscous state formed by means of hydrophilic colloids (e.g., a jelly state formed with gelatin). Furthermore, the dispersion may contain a preservative in order to prevent proliferation of microorganisms during storage.

【0057】

The silver salt of an organic acid solid fine grain dispersion used in the present invention comprises at least a silver salt of an organic acid and water. While the ratio of the silver salt of the organic acid to water is not particularly limited, it must be decided based on rheological characteristics for stable coating and production speed determined by dry moisture content in view of efficient formation of coated films, when the dispersion is used in the coating solution for producing the thermally processed image recording material. The silver salt of the organic acid preferably accounts for from 10-50 weight %, particularly preferably from 10-30 weight % of the entire dispersion.

【0058】

In the present invention, metal ions selected from Ca, Mg, Ce, Al, Zn and Ba are preferably added, in the form of a water-soluble metal salt, to the organic acid silver salt. These metal ions are preferably added in the form of water-soluble salts, not halide compounds. Specifically, they are preferably added in the form of nitrate or sulfate.

【0059】

Time of the addition of the metal ions selected from Ca, Mg, Ce, Al, Zn and Ba is not particularly limited, and they may be added any time. For example, they may be added to the organic acid silver salt liquid preparation, preliminarily added to a reaction mixture, added during or immediately after the formation of the organic acid silver salt, or immediately before the coating, i.e., before or after the formation of coating solution. The amount is preferably 10^{-3} to 10^{-1} mole, particularly preferably 5×10^{-3} to 5×10^{-2} mole, per one mole of the organic acid silver salt.

【0060】

In the following, the production of the thermally processed image recording material using the organic acid silver salt obtained by the preparation method of the present invention will be explained. The thermally processed image recording material can be produced by mixing the water dispersion of the organic acid silver salt obtained by the preparation method of the present invention with that of the

photosensitive silver salt. The mixing ratio between the organic acid silver salt and the photosensitive silver salt is selected depending upon the purpose, but the ratio of the photosensitive silver salt to the organic acid silver salt is in a range of preferably 1–30 mol%, more preferably 3–20 mol%, further preferably 5–15 mol%. It is a method preferably used that when mixed, two or more kinds of water dispersions of organic acid silver salts are mixed with two or more kinds of water dispersions of photosensitive silver salts from the standpoint of adjusting the photographic performance.

【0061】

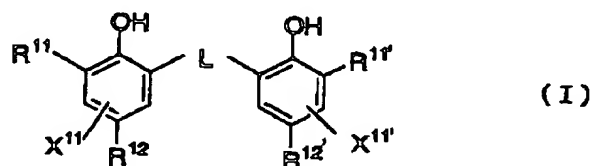
The silver salt of the organic acid in the thermally processed image recording material may be used in any desired amount. However, it is preferably used in an amount of 0.1–5 g/m², more preferably 1–3 g/m², in terms of silver amount.

【0062】

The thermally processed image recording material preferably contains a reducing agent for the organic acid silver salt. The reducing agent for the organic acid silver salt may be any substance (preferably, organic substance) capable of reducing silver ions into silver. Some examples of the reducing agent are described in JP-A-11-65021, paragraphs 0043 to 0045, and EP 0803764A1, from page 7, line 34 to page 18, line 12. The compound expressed by the following formula (I) is preferably used as the reducing agent.

【0063】

【Chemical formula 1】



【0064】

In the formula (I), R¹¹ and R^{11'} each independently denote an alkyl group. R¹² and R^{12'} independently denote a hydrogen atom or a substituent group which can replace the benzene ring. X¹¹ and X^{11'} each independently denote a hydrogen atom or a substituent group which can replace the benzene ring. Each of R¹¹ and X¹¹, R^{11'} and X^{11'}, R¹² and X¹¹, and R^{12'} and X^{11'} may bond to each other to form a ring. L denotes a –S– group or a –CHR¹³–group, and R¹³ denotes a hydrogen atom or an alkyl group.

【0065】

In the formula (I), R^{11} and $R^{11'}$ each independently denote an alkyl group. Specifically, the alkyl group is a substituted or unsubstituted and straight-chain, branched or cyclic alkyl group preferably having 1 to 20 carbons. A substituent group for the alkyl group is not particularly limited, but preferably an aryl group, a hydroxyl group, an alkoxy group, an aryloxy group, alkylthio group, an arylthio group, an acylamino group, a sulfone amide group, a sulfonyl group, a phosphoryl group, an acyl group, a carbomoyl group, an ester group, a halogen atom or the like.

【0066】

More preferably, R^{11} and $R^{11'}$ each independently represent a secondary or tertiary alkyl group having 3–15 carbon atoms, which specifically includes isopropyl group, isobutyl group, t-butyl group, t-amino group, t-octyl group, cyclohexyl group, cyclopentyl group, 1-methylcyclohexyl group, 1-methylcyclopropyl group, etc. Further preferably, the alkyl group is a tertiary alkyl group having 4–12 carbon atoms. Among them, t-butyl group, t-amino group and 1-methylcyclohexyl group are particularly preferable, and t-butyl group is most preferable.

【0067】

R^{12} and $R^{12'}$ independently denote a hydrogen atom or a substituent group which can replace the benzene ring. X^{11} and $X^{11'}$ each independently denote a hydrogen atom or a substituent group which can replace the benzene ring. As the substituent group which can replace the benzene ring, alkyl group, aryl group, halogen atom, alkoxy group, acylamino group, etc. can be recited.

【0068】

R^{12} and $R^{12'}$ each preferably denote an alkyl group having 1–20 carbon atoms, and specifically methyl group, ethyl group, propyl group, butyl group, octyl group, isopropyl group, t-butyl group, t-amyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, methoxymethyl group, methylethyl group or the like. More preferable is methyl group, ethyl group, propyl group, isopropyl group or t-butyl group. X^{11} and $X^{11'}$ preferably each denote hydrogen atom, halogen atom or alkyl group, and particularly preferably hydrogen atom. Each of R^{11} and X^{11} , $R^{11'}$ and $X^{11'}$, R^{12} and X^{11} , and $R^{12'}$ and $X^{11'}$ may bond to each other to form a ring. Such a ring is preferably a 5–7 membered ring, more preferably a saturated 6-membered ring.

【0069】

L is a $-S-$ group or a $-CHR^{13}-$ group, and R^{13} denotes a hydrogen atom or an alkyl group. Specifically, R^{13} is a substituted or unsubstituted and straight-chain,

branched or cyclic alkyl group preferably having 1 to 20 carbons. As specific examples of the unsubstituted alkyl group represented by R^{13} , methyl group, ethyl group, propyl group, butyl group, heptyl group, undecyl group, isopropyl group, 1-ethylpentyl group, 2,4,4-trimethylpentyl group, etc. can be recited. The substituent groups of the substituted alkyl group represented by R^{13} are the same as those of R^{11} and $R^{11'}$.

【0070】

L is preferably $-CHR^{13}$ -group. R^{13} preferably is hydrogen atom or C1-C15 alkyl group. The alkyl group is preferably a primary or secondary alkyl group having 1-8 carbon atoms, more preferably methyl group, ethyl group, n-propyl group, isopropyl group or 2,4,4-trimethylpentyl group, further preferably methyl group, ethyl group, n-propyl group or isopropyl group, particularly preferably methyl group, ethyl group or n-propyl group.

【0071】

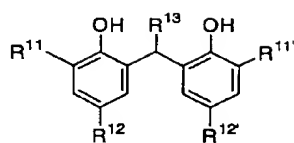
When R^{13} is hydrogen atom, R^{12} and $R^{12'}$ each denote preferably alkyl group having two or more carbon atoms, more preferably alkyl group having 2-5 carbon atoms, further preferably ethyl group or propyl group, most preferably ethyl group. When R^{13} is alkyl group, R^{12} and $R^{12'}$ each denote preferably alkyl group, particularly preferably methyl group.

【0072】

In the following, specific examples of the compounds represented by the following formula (I), but the compounds usable in the invention are not limited thereto.

【0073】

【Chemical formula 2】



	R ¹¹	R ^{11'}	R ¹²	R ^{12'}	R ¹³
I-1	CH ₃	CH ₃	CH ₃	CH ₃	H
I-2	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃
I-3	CH ₃	CH ₃	CH ₃	CH ₃	C ₃ H ₇
I-4	CH ₃	CH ₃	CH ₃	CH ₃	i-C ₃ H ₇
I-5	CH ₃	CH ₃	CH ₃	CH ₃	CH(C ₂ H ₅)C ₄ H ₉
I-6	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH(CH ₃)CH ₂ C(CH ₃) ₃
I-7	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅	H
I-8	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅	i-C ₃ H ₇
I-9	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₃	H
I-10	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₃	i-C ₃ H ₇
I-11	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	H
I-12	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₃
I-13	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	C ₂ H ₅
I-14	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	n-C ₃ H ₇
I-15	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	n-C ₄ H ₉
I-16	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	n-C ₇ H ₁₅
I-17	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	n-C ₁₁ H ₂₃
I-18	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	i-C ₃ H ₇
I-19	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH(C ₂ H ₅)C ₄ H ₉
I-20	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH(CH ₃) ₂

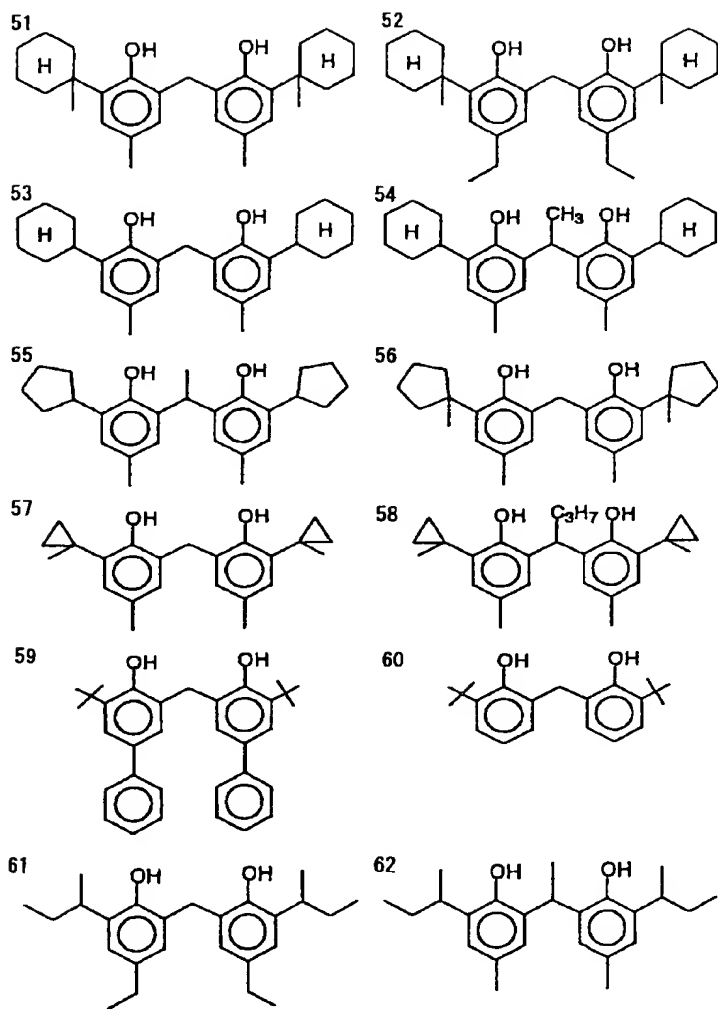
【0074】

【Chemical formula 3】

	R ¹¹	R ^{11'}	R ¹²	R ^{12'}	R ¹³
I-21	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH(CH ₃)CH ₂ C(CH ₃) ₃
I-22	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ OCH ₃
I-23	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH ₂ OCH ₃
I-24	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH ₂ OC ₄ H ₉
I-25	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH ₂ SC ₁₂ H ₂₅
I-26	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	H
I-27	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	CH ₃
I-28	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	n-C ₃ H ₇
I-29	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	i-C ₃ H ₇
I-30	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	CH ₂ CH ₂ OCH ₃
I-31	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₃ H ₇	n-C ₃ H ₇	H
I-32	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₃ H ₇	n-C ₃ H ₇	CH ₃
I-33	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₃ H ₇	n-C ₃ H ₇	n-C ₃ H ₇
I-34	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₄ H ₉	n-C ₄ H ₉	H
I-35	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₄ H ₉	n-C ₄ H ₉	CH ₃
I-36	t-C ₅ H ₁₁	t-C ₅ H ₁₁	CH ₃	CH ₃	H
I-37	t-C ₅ H ₁₁	t-C ₅ H ₁₁	CH ₃	CH ₃	CH ₃
I-38	t-C ₅ H ₁₁	t-C ₅ H ₁₁	C ₂ H ₅	C ₂ H ₅	H
I-39	t-C ₅ H ₁₁	t-C ₅ H ₁₁	C ₂ H ₅	C ₂ H ₅	CH ₃
I-40	i-C ₃ H ₇	i-C ₃ H ₇	CH ₃	CH ₃	H
I-41	i-C ₃ H ₇	i-C ₃ H ₇	CH ₃	CH ₃	n-C ₃ H ₇
I-42	i-C ₃ H ₇	i-C ₃ H ₇	C ₂ H ₅	C ₂ H ₅	H
I-43	i-C ₃ H ₇	i-C ₃ H ₇	C ₂ H ₅	C ₂ H ₅	n-C ₃ H ₇
I-44	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	H
I-45	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	CH ₃
I-46	t-C ₄ H ₉	CH ₃	CH ₃	CH ₃	H
I-47	t-C ₄ H ₉	CH ₃	CH ₃	CH ₃	CH ₃
I-48	t-C ₄ H ₉	CH ₃	CH ₃	CH ₃	n-C ₃ H ₇
I-49	t-C ₄ H ₉	CH ₃	t-C ₄ H ₉	CH ₃	CH ₃
I-50	i-C ₃ H ₇	CH ₃	CH ₃	CH ₃	CH ₃

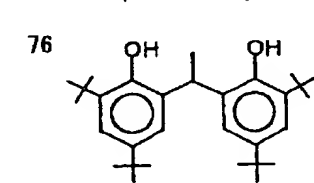
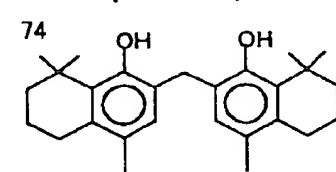
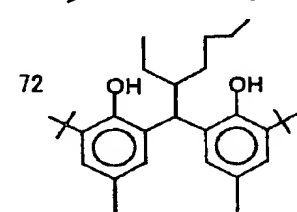
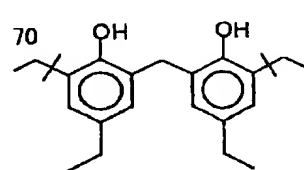
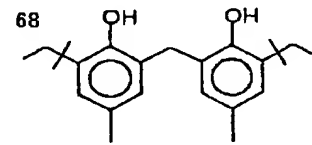
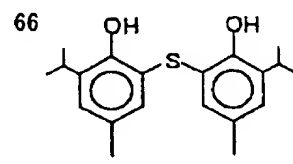
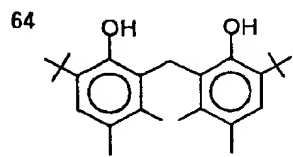
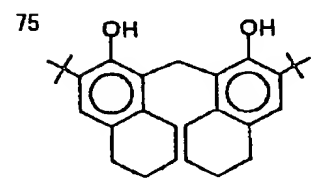
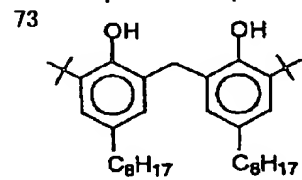
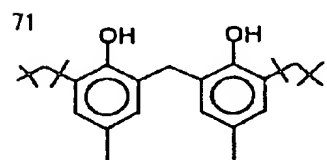
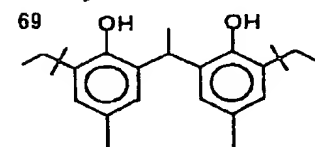
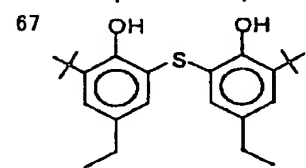
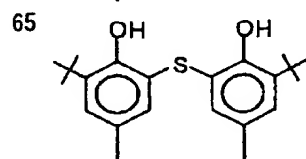
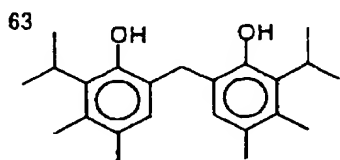
【0075】

【Chemical formula 4】



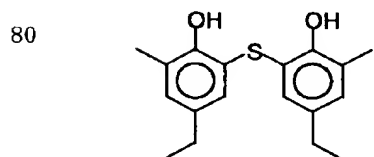
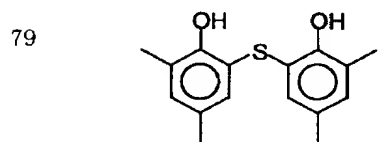
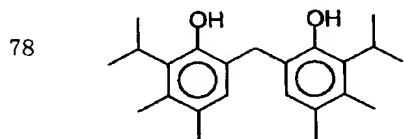
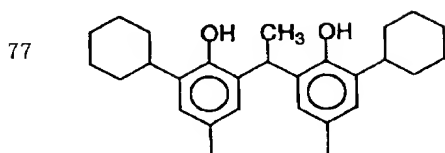
[0076]

[Chemical formula 5]



【0077】

【Chemical formula 6】



【0078】

The addition amount of the reducing agent is preferably 0.01–5.0 g/m², more preferably 0.1–3.0 g/m². The amount of the reducing agent is preferably 5–50 mole %, more preferably 10–40 mole %, per mole of silver on the image-forming layer side. The reducing agent is preferably contained in the image-forming layer. The reducing agent may be added to a coating solution in any form such as solution, emulsion dispersion and solid microparticle dispersion, so as to be contained in the thermally processed image recording material. As a well known emulsion dispersion method, there can be mentioned a method for mechanically preparing an emulsion dispersion by using an oil such as dibutyl phthalate, tricresyl phosphate, glyceryl triacetate or diethyl phthalate, ethyl acetate or cyclohexanone as an auxiliary solvent.

【0079】

Further, as a method for solid microparticle dispersion, there can be mentioned a method for preparing solid microparticle dispersion by dispersing powder of the reducing agent in a suitable solvent such as water using a ball mill, colloid mill, vibration ball mill, sand mill, jet mill and roller mill, or by means of ultrasonic wave. In this operation, protective colloid (e.g., polyvinyl alcohol),

surfactant (e.g., anionic surfactants such as sodium triisopropyl naphthalenesulfonate (mixture of those having three isopropyl groups on different positions)) and so forth may be used. An aqueous dispersion may contain a preservative (e.g., benzisothiazolinone sodium salt).

【0080】

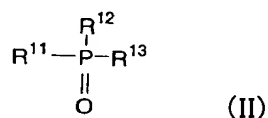
In the thermally processed image recording material, the phenol derivatives represented by the formula (A) mentioned in Japanese Patent Application No. 11-73951 are preferably used as a development accelerator.

【0081】

When the reducing agent has an aromatic hydroxyl group (—OH), in particular when the reducing agent is any of the bisphenols, it is preferable to use together a non-reducing compound having a group that can form a hydrogen bond with the aromatic hydroxyl group. Examples of the group that can form a hydrogen bond with hydroxyl group or amino group include phosphoryl group, sulfoxido group, sulfonyl group, carbonyl group, amido group, an ester group, urethane group, ureido group, a tertiary amino group, a nitrogen-containing aromatic group and so forth. Among them, particularly preferred examples of such a compound are those compounds having phosphoryl group, sulfoxido group, amido group (provided that it does not have >N—H group, but it is blocked like >N—R (R is a substituent other than H)), urethane group (provided that it does not have >N—H group, but it is blocked like >N—R (R is a substituent other than H)), or ureido group (provided that it does not have >N—H group, but it is blocked like >N—R (R is a substituent other than H)). In the present invention, particularly preferred hydrogen bond-forming compounds are compounds represented by the following formula (II).

【0082】

【Chemical formula 7】



【0083】

In the formula (II), R²¹, R²² and R²³ each independently represent an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group or a heterocyclic group, and these groups may or may not have one or more substituents. Two of R²¹, R²² and R²³ may be bonded together to form a ring.

When R^{21} , R^{22} and R^{23} have one or more substituents, they can be selected from a halogen atom, an alkyl group, an aryl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an alkylthio group, an arylthio group, a sulfonamide group, an acyloxy group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, a phosphoryl group and so forth, and they are preferably selected from an alkyl group and an aryl group. Specific examples thereof are methyl group, ethyl group, isopropyl group, t-butyl group, t-octyl group, phenyl group, 4-alkoxyphenyl group, 4-acyloxyphenyl group and so forth.

[0084]

Specific examples of the groups represented by R^{21} , R^{22} and R^{23} include a substituted or unsubstituted alkyl group such as methyl group, ethyl group, butyl group, octyl group, dodecyl group, isopropyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, phenethyl group and 2-phenoxypropyl group; a substituted or unsubstituted aryl group such as phenyl group, cresyl group, xylyl group, naphthyl group, 4-t-butylphenyl group, 4-t-octylphenyl group, 4-anisidyl group and 3,5-dichlorophenyl group; a substituted or unsubstituted alkoxy group such as methoxy group, ethoxy group, butoxy group, octyloxy group, 2-ethylhexyloxy group, 3,5,5-trimethylhexyloxy group, dodecyloxy group, cyclohexyloxy group, 4-methylcyclohexyloxy group and benzyloxy group; a substituted or unsubstituted aryloxy group such as phenoxy group, cresyloxy group, isopropylphenoxy group, 4-t-butylphenoxy group, naphthoxy group and biphenyloxy group; a substituted or unsubstituted amino group such as amino group, dimethylamino group, diethylamino group, dibutylamino group, dioctylamino group, N-methyl-N-hexylamino group, dicyclohexylamino group, diphenylamino group and N-methyl-N-phenylamino group; a heterocyclic group such as 2-pyridyl group, 4-pyridyl group, 2-furanyl group, 4-piperidinyl group, 8-quinolyl group and 5-quinolyl group, and so forth.

[0085]

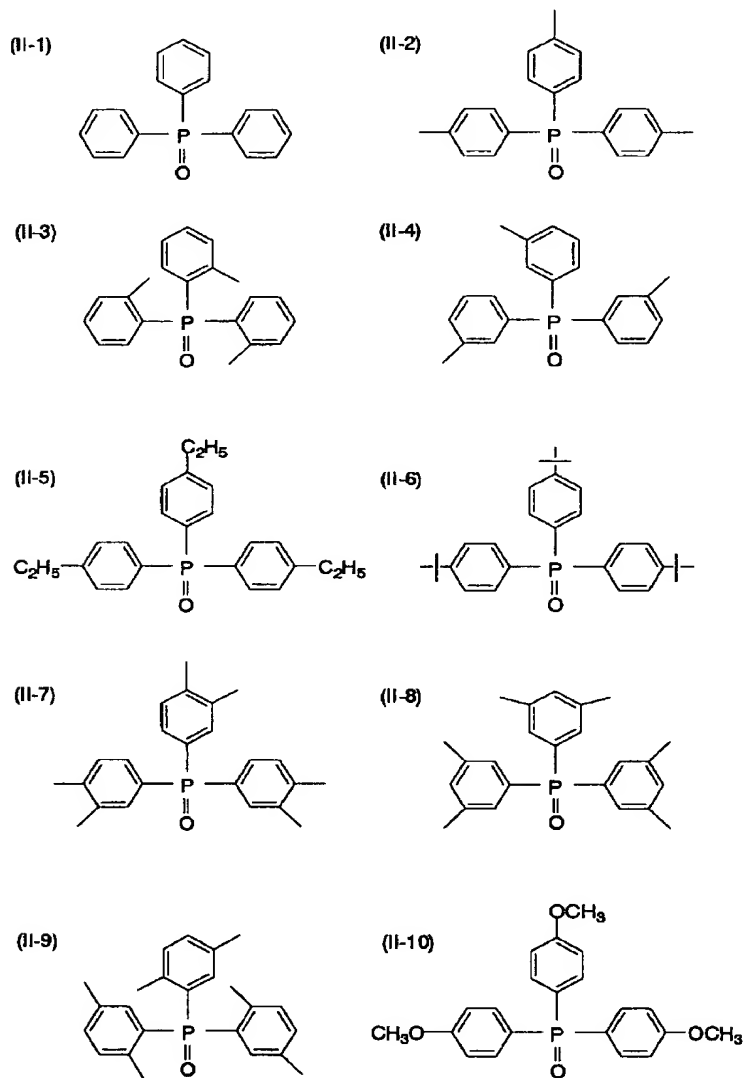
R^{21} , R^{22} and R^{23} are preferably selected from an alkyl group, an aryl group, an alkoxy group and an aryloxy group. It is preferred that one or more of R^{21} , R^{22} and R^{23} should be selected from an alkyl group and an aryl group, and it is more preferred that two or more of R^{21} , R^{22} and R^{23} should be selected from an alkyl group and an aryl group. In view of availability at low cost, it is preferred that R^{21} , R^{22} and R^{23} should be the same groups.

[0086]

Specific examples of the compound represented by the formula (II) will be shown below. However, the compounds that can be used for the present invention are not limited to these examples.

【0087】

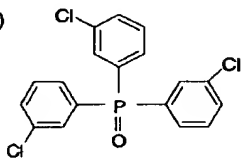
【Chemical formula 8】



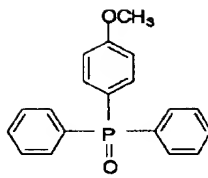
【0088】

【Chemical formula 9】

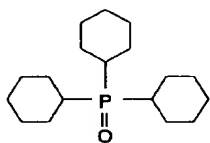
(II-11)



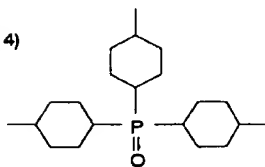
(II-12)



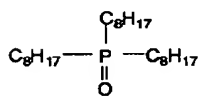
(II-13)



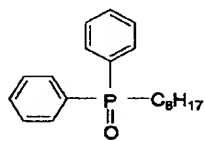
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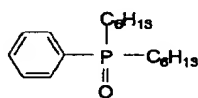
(II-15)



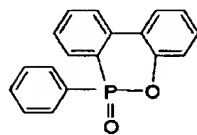
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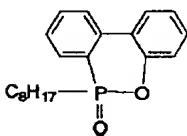
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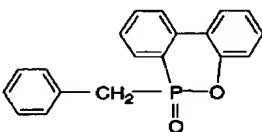
(II-18)



(II-19)



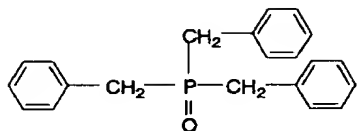
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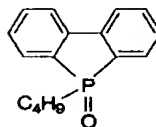
【0089】

【Chemical formula 10】

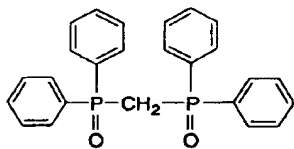
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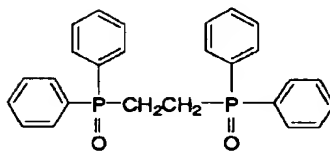
(II-22)



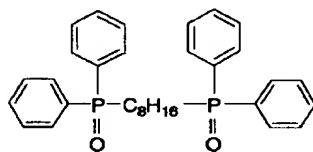
(II-23)



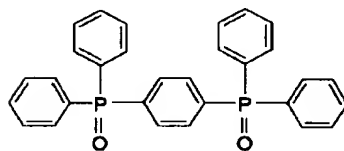
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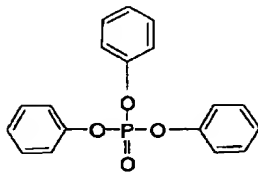
(II-25)



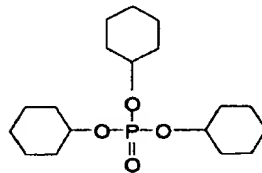
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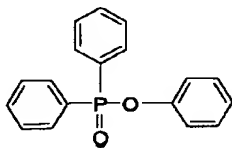
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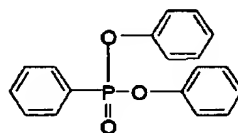
(II-28)



(II-29)



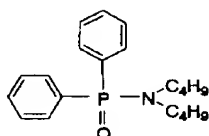
(II-30)



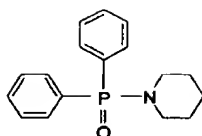
【0090】

【Chemical formula 11】

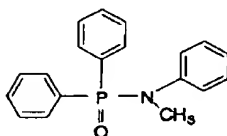
(II-31)



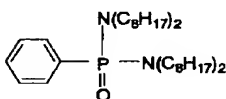
(II-32)



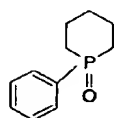
(II-33)



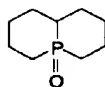
(II-34)



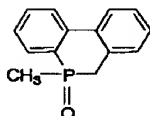
(II-35)



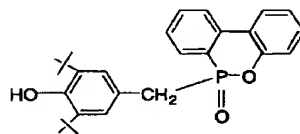
(II-36)



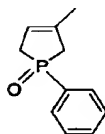
(II-37)



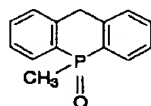
(II-38)



(II-39)



(II-40)



【0091】

In the same as with the reducing agent, the hydrogen bond-forming compound used in the present invention may be contained in a coating liquid in any form such as solution, emulsion dispersion and solid microparticle dispersion, so as to be contained in the thermally processed image recording material. Since the hydrogen bond-forming compound used in the present invention forms a hydrogen bond-based complex in a solution with a compound having a phenolic hydroxyl group or amino group through hydrogen bond, it can be isolated as crystals of such a complex depending on the combination of the reducing agent. Crystal powder isolated in such a manner is particularly preferably used as solid microparticle dispersion in order to obtain stable performance. Further, it is also preferable to mix the reducing agent and the hydrogen bond-forming compound as powders and allow them to form a complex during dispersion operation using a suitable dispersing agent in a sand grinder mill or the like. The use amount of the hydrogen

bond-forming compound is preferably 1–200 mol%, more preferably 10–150 mol%, further preferably 30–100 mol% relative to the reducing agent.

【0092】

The photosensitive silver halide that can be used for the present invention is not particularly limited as for the halogen composition, and silver chloride, silver chlorobromide, silver bromide, silver iodobromide, and silver chloriodobromide may be used. The halide composition may have a uniform distribution in the photosensitive silver halide grains, or the compositions may change stepwise or continuously in the grains. Silver halide grains having a core/shell structure may be preferably used. Core/shell grains having preferably a double to quintuple structure, more preferably a double to quadruple structure may be used. A technique for localizing silver bromide on the surface of silver chloride or silver chlorobromide grains may also be preferably used.

【0093】

Methods for the preparation of the photosensitive silver halide are well known in the art, and there can be used, for example, the methods described in Research Disclosure, No. 17029 (June, 1978) and U.S. Patent No. 3,700,458. More specifically, a method can be used which comprises preparing photosensitive silver halide by addition of a silver-supplying compound and a halogen-supplying compound to a solution of gelatin or other polymer, and then mixing the resulting grains with a silver salt of an organic acid. The methods disclosed in JP-A-119374, paragraphs 0217 to 0224, Japanese Patent Application Nos. 11-98708 and 11-84182 are also preferred.

【0094】

As for a grain size of the photosensitive silver halide, smaller grains are desirable to prevent cloudiness after image formation. Specifically, the grain size may preferably be not greater than 0.20 μm , more preferably 0.01–0.15 μm , further preferably 0.02–0.12 μm . The term “grain size” used herein means a diameter of a circle having the same area as that of a projected area of a halogen silver grain (where silver halide grains are tabular grains, a projected area of the main surface of the tabular grain).

【0095】

Examples of the form of silver halide grains include a cubic form, octahedral form, tabular form, spherical form, rod-like form and potato-like form. In particular, cubic grains are preferred. Silver halide grains having round corners

are also preferably used. Surface index (Miller index) of outer surfaces of the photosensitive silver halide grains is not particularly limited. However, it is desirable that the [100] face, which can achieve high spectral sensitizing efficiency when a spectral sensitizing dye adsorbs on the grains, should be present in a high proportion. The proportion of the [100] face may be preferably not lower than 50%, more at least 65%, still more preferably at least 80%. The proportion of Miller index [100] face can be determined using the method described in T. Tani, J. Imaging Sci., 29, 165 (1985), which utilizes the difference in adsorption of a sensitizing dye between [111] face and [100] face in the spectral sensitizing dye.

【0096】

Silver halide grains having hexacyano-metal complex on their outermost surfaces are preferably used. Specific examples of the hexacyano-metal complex include $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Ru}(\text{CN})_6]^{4-}$, $[\text{Os}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{CN})_6]^{3-}$, $[\text{Ir}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{CN})_6]^{3-}$, $[\text{Re}(\text{CN})_6]^{3-}$ and so forth. In the present invention, hexacyano-Fe complexes are preferred.

【0097】

Since the hexacyano-metal complex exists in the form of an ion in an aqueous solution, its counter cation is not critical. However, it is preferable to use ions readily mixed with water and suitable for the precipitation operation of silver halide emulsions, for example, alkali metal ions such as sodium ion, potassium ion, rubidium ion, cesium ion and lithium ion, ammonium ions, alkylammonium ions (e.g., tetramethylammonium ions, tetraethylammonium ions, tetrapropylammonium ions, tetra-

(n-butyl)ammonium ions) and so forth.

【0098】

The hexacyano-metal complex may be added to silver halide grains in the form of a solution in water or in a mixed solvent of water and an organic solvent miscible with water (for example, alcohols, ethers, glycols, ketones, esters, amides etc.), or in the form of a mixture thereof with gelatin.

【0099】

The amount of the hexacyano-metal complex is preferably 1×10^{-5} mole to 1×10^{-2} mole, more preferably 1×10^{-4} mole to 1×10^{-3} mole, per mol of silver.

【0100】

In order to make the hexacyano-metal complex exist on the outermost surfaces of silver halide grains, the hexacyano-metal complex is directly added

before completion of the grain formation process, i.e., after the addition of an aqueous silver nitrate solution used for the formation of silver halide grains and before chemical sensitization process where chalcogen sensitization with sulfur, selenium or tellurium or noble metal sensitization with gold or the like is performed, during washing with water or dispersion operation or immediately before the chemical sensitization. To prevent growth of the silver halide grains, it is desirable that the hexacyano-metal complex is added to the grains immediately after the grains are formed, and the complex is added before the grain formation process is finished.

【00101】

The addition of the hexacyano-metal complex may be started after 96 weight % of the total of silver nitrate for grain formation has been added. More preferably, it is added after 98 weight of silver nitrate, particularly preferably after 99 weight % of silver nitrate has been added.

【0102】

If the hexacyano-metal complex is added after addition of aqueous solution of silver nitrate in which the formation of silver halide grains is almost completed, the hexacyano-metal complex can be adsorbed onto the outermost surfaces of the silver halide grains, and most of the complex forms a hardly-soluble salt with silver ions existing on the surfaces of the grains. Such a silver salt of hexacyano-iron(II) is a salt more hardly soluble than AgI, and therefore fine grains formed are prevented from being dissolved again. Thus, it becomes possible to produce fine silver halide grains having a small grain size.

【0103】

The photosensitive silver halide grains may contain a metal of Group VIII to Group X in the periodic table of elements (including Group I to Group XVIII) or metal complex thereof. The metal of Group VIII to X of the periodic table or the center metal of the metal complex is preferably rhodium, ruthenium or iridium. The metal complex may be used alone, or two or more complexes of the same or different metals may also be used in combination. The metal complex content is preferably from 1×10^{-9} to 1×10^{-3} mole per mole of silver. Such heavy metals and metal complexes as well as addition method therefor are described in JP-A-7-225449, JP-A-11-65021, paragraphs 0018 to 0024, and JP-A-11-119374, paragraphs 0227 to 0240.

【0104】

Further, metal complexes that can be contained in the silver halide grains used for the present invention (e.g., $[\text{Fe}(\text{CN})_6]^{4-}$), silver halide emulsion-desalting methods and chemical sensitization methods are described in JP-A-11-84574, paragraphs 0046 to 0050, JP-A-11-65021, paragraphs 0025 to 0031, and JP-A-11-119374, paragraphs 0242 to 0250.

【0105】

As gelatin contained in the photosensitive silver halide emulsion, various kinds of gelatin may be used. In order to obtain good dispersion state of the photosensitive silver halide emulsion in a coating solution containing a silver salt of an organic acid, low molecular weight gelatin having a molecular weight of 500-60,000 is preferably used. While such low molecular weight gelatin may be used during the grain formation or the dispersion operation after the desalting treatment, it is preferably used during the dispersion operation after the desalting treatment.

【0106】

As a sensitizing dye that can be used for the present invention, there can be advantageously selected those sensitizing dyes which can spectrally sensitize silver halide grains within a desired wavelength range after they are adsorbed by the silver halide grains and have spectral sensitivity suitable for spectral characteristics of the light source to be used for exposure. Such sensitizing dyes and addition methods therefor are described in JP-A-11-65021, paragraphs 0103 to 0109, JP-A-10-18657 as for the compounds represented by the formula (II), JP-A-11-119347 as for the dyes represented by the formula (I) and paragraph 0106, U.S. Patent Nos. 5,510,236, 3,871,887 as for the dyes disclosed in Example 5, JP-A-2-96131, JP-A-59-48753 as for the dyes disclosed therein and EP 0803764A1, page 19, line 38 to page 20, line 35, Japanese Patent Application Nos. 2000-86865, 2000-102560 and so forth. These dyes may be used each alone or in any combination of two or more of them. The sensitizing dye is added to the silver halide emulsion preferably during the period after the desalting step and before the coating step, more preferably during the period after the desalting step and before the start of the chemical ripening. While the amount of the sensitizing dye used in the present invention may be selected to be a desired amount depending on the performance including sensitivity and fog, it is preferably 10^{-6} to 1 mole, more preferably 10^{-4} to 10^{-1} mole, per mole of silver halide in the image-forming layer.

【0107】

A supersensitizer can be used for the thermally processed image recording material in order to improve spectral sensitization efficiency. Examples of the supersensitizer include the compounds disclosed in EP587338A, U.S. Patent Nos. 3,877,943, 4,873,184, JP-A-5-341432, JP-A-11-109547, JP-A-10-111543 and so forth.

【0108】

Photosensitive silver halide grains are preferably subjected to chemical sensitization by sulfur sensitization, selenium sensitization or tellurium sensitization. Any known compounds can be preferably used for such sulfur, selenium or tellurium sensitization, and for example, the compounds described in JP-A-7-128768 and so forth are usable for that purpose. Tellurium sensitization is particularly preferred, and the compounds described in JP-A-11-65021, paragraph 0030 and the compounds of formulas (II), (III) and (IV) given in JP-A-5-313284 are more preferred.

【0109】

The chemical sensitization may be performed at any time so long as it is performed after the formation of the grains and before the coating. It may be performed after desalting and before the spectral sensitization, simultaneously with the spectral sensitization, after the spectral sensitization, immediately before the coating, or the like. It is particularly preferably performed after spectral sensitization. The amount of the sulfur, selenium or tellurium sensitizer varies depending on the type of the silver halide grains to be used, the condition for chemical ripening etc., but may fall generally between 10^{-8} and 10^{-2} mole, preferably between 10^{-7} and 10^{-3} mole or so, per mol of the silver halide. Although the conditions for the chemical sensitization are not particularly limited, in general, pH is in the range of 5-8, the pAg in the range of 6-11, and the temperature in the range of 40-95°C. The silver halide emulsion may be added with a thiosulfonic acid compound according to the method disclosed in EP293917A.

【0110】

In the thermally processed image recording material, one kind of photosensitive silver halide emulsion may be used or two or more different emulsions (for example, those having different average grain sizes, different halogen compositions, different crystal habits or different chemical sensitization conditions) may be used in combination. By using plural photosensitive silver halides having

different sensitivities, contrast can be controlled. Examples of the techniques concerning this respect include those mentioned in JP-A-57-119341, JP-A-53-106125, JP-A-47-3929, JP-A-48-55730, JP-A-46-5187, JP-A-50-73627, JP-A-57-150841 and so forth. Each emulsion preferably has sensitivity difference of 0.2 log E or higher for other emulsions.

【0111】

The amount of the photosensitive silver halide is preferably 0.03–0.6 g/m², more preferably 0.05–0.4 g/m², most preferably 0.1–0.4 g/m², as the amount of coated silver per 1 m² of the thermally processed image recording material. The amount of the photosensitive silver halide per mole of the silver salt of an organic acid is preferably from 0.01–0.5 mole, more preferably from 0.02–0.3 mole.

【0112】

Methods and conditions for mixing photosensitive silver halide and a silver salt of an organic acid, which are separately prepared, are not particularly limited so long as the effect of the present invention can be attained satisfactorily. Examples thereof include, for example, a method of mixing silver halide grains and a silver salt of an organic acid after completion of respective preparations by using a high-speed stirring machine, ball mill, sand mill, colloid mill, vibrating mill, homogenizer or the like, or a method of preparing a silver salt of an organic acid by mixing a photosensitive silver halide obtained separately at any time during the preparation of the silver salt of an organic acid. For the mixing of them, mixing two or more kinds of aqueous dispersions of the silver salt of an organic acid and two or more kinds of aqueous dispersions of the photosensitive silver salt is preferably used for controlling photographic properties.

【0113】

Preferred addition time point for the silver halide into the coating solution for image-forming layer resides in a period of from 180 minutes before the coating to immediately before the coating, preferably 60 minutes to 10 seconds before the coating. However, the method and conditions for mixing are not particularly limited so long as the effects of the present invention are sufficiently exhibited. Specific examples of the mixing method include a method in which the mixing is performed in a tank designed so that a desired average residence time therein can be obtained, which residence time is calculated from addition flow rate and feeding amount to a coater, a method utilizing a static mixer described in N. Harnby, M.F. Edwards, A.W. Nienow, "Ekitai Kongo Gijutsu (Techniques for Mixing Liquids)", translated by Koji

Takahashi, Chapter 8, Nikkan Kogyo Shinbunsha, 1989 and so forth.

【0114】

The binder of the layer containing the silver salt of an organic acid may be any polymer. Preferred binders are those that are transparent or translucent, and generally colorless. The binder may consist of, for example, a naturally occurring resin, polymer or copolymer, synthetic resin, polymer or copolymer or other media that can form a film, such as gelatins, rubbers, poly(vinyl alcohols), hydroxyethyl celluloses, cellulose acetates, cellulose acetate butyrates, poly(vinylpyrrolidones), casein, starch, poly(acrylic acids), poly(methyl methacrylates), poly(vinyl chlorides), poly(methacrylic acids), styrene/maleic anhydride copolymers, styrene/acrylonitrile copolymers, styrene/butadiene copolymers, poly(vinyl acetals) (e.g., poly(vinyl formal), poly(vinyl butyral)), poly(esters), poly(urethanes), phenoxy resin, poly(vinylidene chlorides), poly(epoxides), poly(carbonates), poly(vinyl acetates), poly(olefins), cellulose esters and poly(amides). The binder may be formed from water, organic solvent or emulsion by coating it.

【0115】

If the layer containing the silver salt of an organic acid is formed by using a coating solution containing 30 weight % or more of water based on a total solvent, further, if the binder of the layer containing the silver salt of an organic acid is soluble or dispersible in an aqueous solvent (water solvent), in particular, if a coating solution containing a polymer latex having an equilibrated moisture content of 2 weight % or less at 25°C and relative humidity of 60% is used, the performance is improved. In the most preferred embodiment, the polymer latex is prepared to have an ion conductivity of 2.5 mS/cm or less. An example of a method for preparing such polymer latex includes a method comprising synthesizing a polymer and then purifying the polymer by using a functional membrane for separation.

【0116】

The aqueous solvent in which the above binder is soluble or dispersible is water or water mixed with 70 weight % or less of a water-miscible organic solvent. Examples of the water-miscible organic solvent include, for example, alcohols such as methyl alcohol, ethyl alcohol and propyl alcohol; cellosolves such as methyl cellosolve, ethyl cellosolve and butyl cellosolve; ethyl acetate, dimethylformamide and so forth.

【0117】

The term “aqueous solvent” used herein also encompasses systems in

which a polymer is not thermodynamically dissolved but is present in a so-called dispersed state.

【0118】

The definition “equilibrated moisture content at 25°C and relative humidity of 60%” used herein can be represented by the following equation, in which W^1 indicates the weight of a polymer at humidity-conditioned equilibrium in an atmosphere of 25°C and relative humidity of 60%, and W^0 indicates the absolute dry weight of the polymer at 25°C.

Equilibrated moisture content at 25°C and relative humidity of 60% = $[(W^1 - W^0)/W^0] \times 100$ (weight %)

【0119】

As for details of the definition of moisture content and methods for measurement, for example, Lecture of Polymer Engineering, 14, Test Methods for Polymer Materials (Polymer Society of Japan, Chijin Shokan) can be referred to.

【0120】

The equilibrated moisture content at 25°C and relative humidity of 60% of the binder polymer is preferably 2 weight % or less, more preferably from 0.01–1.5 weight %, most preferably from 0.02–1 weight %.

【0121】

Polymers dispersible in aqueous solvents are particularly preferred as the binder polymer. Examples of the dispersed state include, for example, latex in which fine particles of water-insoluble, hydrophobic polymer are dispersed, and a system in which polymer molecules are dispersed in a molecular state or as micelles, both of which are preferred. Dispersed particles preferably have a mean particle size of around 1–50000 nm, more preferably around 5–1000 nm. Particle size distribution of the dispersed particles is not particularly limited, and either those having a broad particle size distribution or those having monodispersed particle size distribution may be used.

【0122】

In preferred embodiments of the polymer dispersible in an aqueous solvent, hydrophobic polymers such as acrylic polymers, polyesters, rubbers (e.g., SBR resins), polyurethanes, polyvinyl chlorides, polyvinyl acetates, polyvinylidene chlorides, and polyolefins can preferably be used. The polymers may be linear, branched or crosslinked. They may be so-called homopolymers in which a single kind of monomer is polymerized, or copolymers in which two or more different kinds

of monomers are polymerized. The copolymers may be random copolymers or block copolymers. The polymers may have a number average molecular weight of 5,000 to 1,000,000, preferably from 10,000 to 200,000. Polymers having a too small molecular weight fail to give sufficient mechanical strength of the emulsion layer, and those having a too large molecular weight yield bad film forming property, and both of which are not preferred.

【0123】

Specific examples of the preferred polymer latex are mentioned below. They are expressed with the constituent monomers. The numerals parenthesized indicate the contents in terms of weight %. The molecular weights are number average molecular weights.

【0124】

P-1: Latex of -MMA(70)-EA(27)-MAA(3)-

(molecular weight: 37000)

P-2: Latex of -MMA(70)-2EHA(20)-St(5)-AA(5)-

(molecular weight: 40000)

P-3: Latex of -St(50)-Bu(47)-MMA(3)-

(molecular weight: 45000)

P-4: Latex of -St(68)-Bu(29)-AA(3)-

(molecular weight: 60000)

P-5: Latex of -St(71)-Bu(26)-AA(3)-

(molecular weight: 60000)

P-6: Latex of -St(70)-Bu(27)-IA(3)-

(molecular weight: 120000)

P-7: Latex of -St(75)-Bu(24)-AA(1)-

(molecular weight: 108000)

P-8: Latex of -St(60)-Bu(35)-DVB(3)-MAA(2)-

(molecular weight: 150000)

P-9: Latex of -St(70)-Bu(25)-DVB(2)-AA(3)-

(molecular weight: 280000)

P-10: Latex of -VC(50)-MMA(20)-EA(20)-AN(5)-AA(5)-

(molecular weight: 80000)

P-11: Latex of -VDC(85)-MMA(5)-EA(5)-MAA(5)-

(molecular weight: 67000)

P-12: Latex of -Et(90)-MAA(10)-

(molecular weight: 12000)

P-13: Latex of -St(70)-2EHA(27)-AA(3)-

(molecular weight: 130000)

P-14: Latex of -MMA(63)-EA(35)-AA(2)-

(molecular weight: 33000)

【0125】

Abbreviations used for the constituent monomers are as follows:

MMA: methyl methacrylate

EA: ethyl acrylate

MAA: methacrylic acid

2EHA: 2-ethylhexyl acrylate

St: styrene

Bu: butadiene

AA: acrylic acid

DVB: divinylbenzene

VC: vinyl chloride

AN: acrylonitrile

VDC: vinylidene chloride

Et: ethylene

IA: itaconic acid

【0126】

The polymer latexes mentioned above are also commercially available, and those mentioned below can be used, for example. Examples of acrylic polymers are CEBIAN A-4635, 46583, 4601 (all from Daicel Chemical Industries), Nipol Lx811, 814, 821, 820, 857 (all from Nippon Zeon) etc.; examples of polyesters are FINETEX ES650, 611, 675, 850 (all from Dai-Nippon Ink & Chemicals), WD-size, WMS (both from Eastman Chemical) etc.; examples of polyurethanes are HYDRAN AP10, 20, 30, 40 (all from Dai-Nippon Ink & Chemicals) etc.; examples of rubbers are LACSTAR 7310K, 3307B, 4700H, 7132C (all from Dai-Nippon Ink & Chemicals), Nipol Lx416, 410, 438C, 2507 (all from Nippon Zeon) etc.; examples of polyvinyl chloride polymers are G351, G576 (both from Nippon Zeon) etc.; examples of polyvinylidene chloride polymers are L502, L513 (both from Asahi Chemical Industry) etc.; examples of polyolefin polymers are CHEMIPPEARL S120, SA100 (both from Mitsui Petrochemical) etc. These polymer latexes may be used each alone, or two or more kinds of them may be blended as required.

【0127】

As the polymer latex, styrene/butadiene copolymer latex is preferred. In the styrene/butadiene copolymer, the weight ratio of styrene monomer units and butadiene monomer units is preferably 40:60 to 95:5. The ratio of the styrene monomer units and the butadiene monomer units preferably account for from 60-99 weight % of the copolymer. The preferred range of the molecular weight of the copolymer is similar to that mentioned above.

【0128】

Preferable examples of styrene/butadiene copolymer latexes include the aforementioned P-3 to P-8, commercially available products, LACSTAR-3307B, 7132C, Nipol Lx416 and so forth.

【0129】

The latex has a glass transition temperature (T_g) within the range of 10-80° C, more preferably in the range of 20-60° C. When a blend of two or more kinds of polymers having different glass transition temperatures is used, it is preferred that its weight average T_g should fall within the aforementioned range.

【0130】

The layer containing silver salt of an organic acid of the thermally processed image recording material may optionally contain a hydrophilic polymer such as gelatin, polyvinyl alcohol, methyl cellulose, hydroxypropyl cellulose and carboxymethyl cellulose. The addition amount of the hydrophilic polymer is preferably 30 weight % or less, more preferably 20 weight % or less, of the total binder in the layer containing silver salt of the organic acid.

【0131】

The layer containing silver salt of an organic acid (i.e., image-forming layer) is preferably formed by using polymer latex. The amount of the binder in the layer containing silver salt of an organic acid is such an amount that the weight ratio of total binder/silver salt of an organic acid should be 1/10 to 10/1, more preferably 1/5 to 4/1.

【0132】

The layer containing silver salt of an organic acid usually also serves as an image-forming layer (photosensitive layer, emulsion layer) containing a photosensitive silver salt, that is, a photosensitive silver halide. In such a case, the weight ratio of total binder/silver halide is preferably 5-400, more preferably 10-200.

【0133】

The total amount of the binder in the image-forming layer is preferably 0.2–30 g/m², more preferably 1–15 g/m². The image-forming layer may optionally contain a crosslinking agent for crosslinking, a surfactant for improving coating property and so forth.

【0134】

The solvent for the coating solution for the layer containing silver salt of an organic acid (for simplicity, solvents and dispersion media are collectively referred to as solvent) is an aqueous solvent containing at least 30 weight % of water. As for components other than water, any water-miscible organic solvents including, for example, methyl alcohol, ethyl alcohol, isopropyl alcohol, methyl cellosolve, ethyl cellosolve, dimethylformamide, ethyl acetate and so forth may be used. The water content of the solvent for the coating solution is preferably at least 50 weight %, more preferably at least 70 weight %. Preferred examples of the solvent composition are water, water/methyl alcohol = 90/10, water/methyl alcohol = 70/30, water/methyl alcohol/dimethylformamide = 80/15/5, water/methyl alcohol/ethyl cellosolve = 80/10/5, water/methyl alcohol/isopropyl alcohol = 85/10/5 and so forth (numerals indicate weight %).

【0135】

As antifoggants, stabilizers and stabilizer precursors that can be used for the present invention, there can be mentioned, for example, those mentioned in JP-A-10-62899, paragraph 0070 and EP0803764A1, from page 20, line 57 to page 21, line 7. Antifoggants preferably used for the present invention are organic halides. Examples thereof include, for example, those disclosed in JP-A-11-65021, paragraphs 0111 to 0112. Particularly preferred are the organic polyhalogenated compounds represented by the formula (P) mentioned in Japanese Patent Application No. 11-87297, and the organic polyhalogenated compounds represented by the formula (II) mentioned in JP-A-10-339934.

【0136】

In the present invention, a polyhalogen compound represented by the following formula (III) is preferably used as the antifoggant.



in which Q denotes an alkyl group, an aryl group or a heterocyclic group, Y denotes a divalent connecting group, n denotes a figure of 0 or 1, Z¹ and Z² each independently denote a halogen atom, and X denotes a hydrogen atom or an

electron-attracting group. The alkyl group, the aryl group or the heterocyclic group represented by Q may each have a substituent group.

【0137】

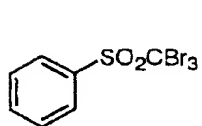
In the formula (III), Q preferably denotes a phenyl group which is replaced by an electron-attracting group having a positive value of a Hammett σ_p . Specific Examples of the electron-attracting group as the substituent group are cyano group, alkoxy carbonyl group, aryloxy carbonyl group, carbamoyl group, sulfamoyl group, alkyl sulfonium group, aryl sulfonyl group, sulfoxide group, acyl group, heterocyclic group, halogen atom, halogenated alkyl group, phosphoryl group and so forth. The σ_p value is preferably 0.2–2.0, more preferably 0.4–1.0. As the electron-attracting group, carbamoyl group, alkoxy carbonyl group, alkyl sulfonium group and alkyl phosphoryl group are particularly preferable. Among them, carbamoyl group is most preferable.

【0138】

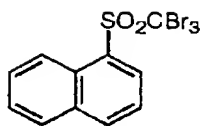
Specific examples of the polyhalogen compound represented by the formula (III) will be shown below. However, the compounds that can be used for the present invention are not limited to them.

【0139】

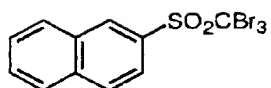
【Chemical formula 12】



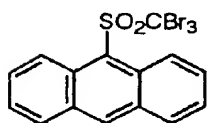
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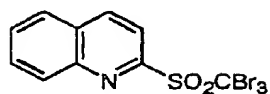
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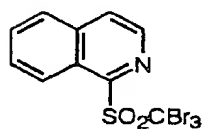
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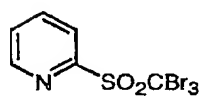
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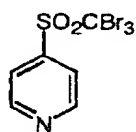
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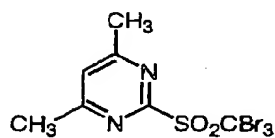
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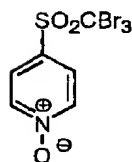
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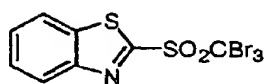
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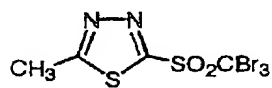
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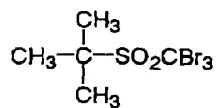
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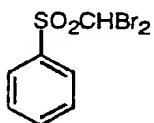
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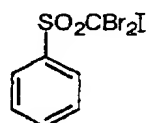
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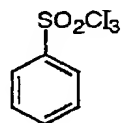
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(P-14)



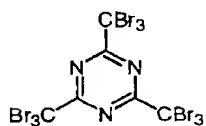
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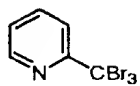
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【0140】

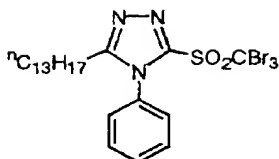
【Chemical formula 13】



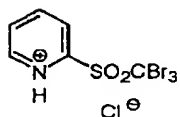
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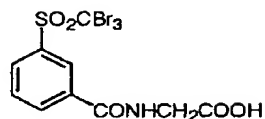
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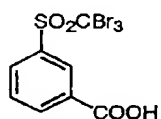
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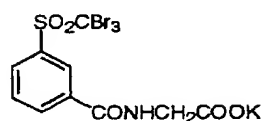
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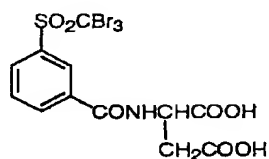
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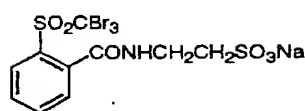
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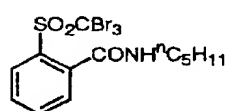
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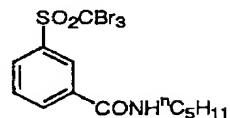
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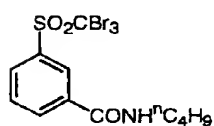
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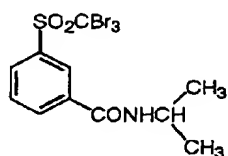
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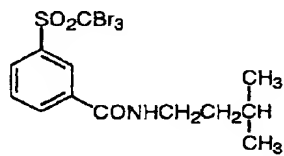
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(P-28)



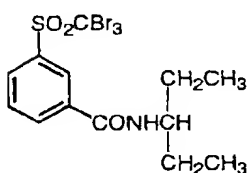
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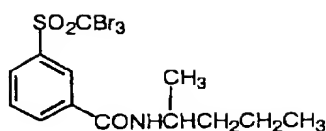
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【0141】

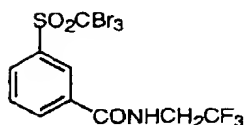
【Chemical formula 14】



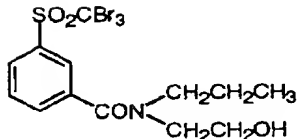
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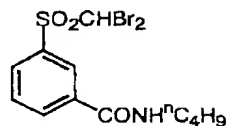
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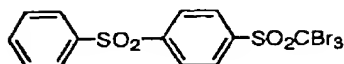
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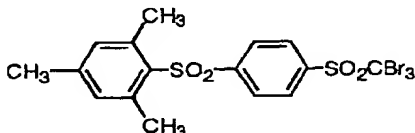
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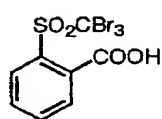
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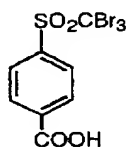
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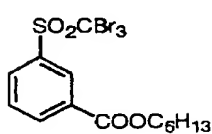
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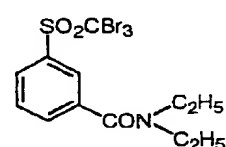
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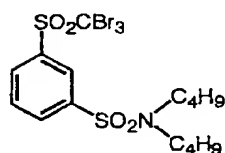
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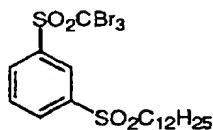
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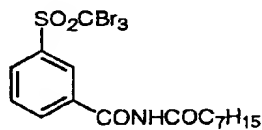
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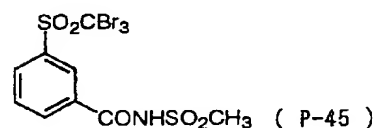
(P-42)



(P-43)



(P-44)



(P-45)

【0142】

It is preferable to use the polyhalogen compound having the formula (III) in an amount of 10^{-1} to 1 mol, more preferably 10^{-3} to 0.8 mol, further preferably 5×10^{-3} to 0.5 mol per one mole of the non-photosensitive silver salt of the image-forming layer. In order to incorporate the antifoggant into the above thermally processed image recording material, a method is recited, which incorporates the above reducing agent into the material. A fine solid dispersion is also preferably added to the antifoggant.

【0143】

Other examples of the antifoggant include the mercury(II) salts described in JP-A-11-65021, paragraph 0113, the benzoic acids described in the same, paragraph 0114, the salicylic acid derivatives represented by the formula (Z) mentioned in Japanese Patent Application No. 11-87297, the formalin scavenger compounds represented by the formula (S) mentioned in Japanese Patent Application No. 11-23995, triazine compounds mentioned in JP-A-11-352624, Claim 9, compounds represented by the formula (III) mentioned in JP-A-6-11791, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and so forth.

【0144】

The thermally processed image recording material may contain an azolium salt for prevention of fog. Examples of the azolium salt include, for example, the compounds of the formula (XI) disclosed in JP-A-59-193447, the compounds disclosed in JP-B-55-12581 and the compounds of the formula (II) disclosed in JP-A-60-153039. While the azolium salt may be added in any site of the thermally processed image recording material, it is preferably added in a layer on the side of an image-forming layer, more preferably in the layer containing silver salt of an organic acid. The azolium salt may be added at any time during the preparation of the coating solution. When the azolium salt is added to the layer containing silver salt of an organic acid, the azolium salt may be added at any time during the period of from the preparation of the silver salt of an organic acid to the preparation of the coating solution. A time during the period after the preparation of the silver salt of an organic acid and immediately before coating is preferred. The azolium salt may be added as any form such as powder, solution and microparticle dispersion. The salt may also be added as a solution prepared by mixing the salt with other additives such as a sensitizing dye, reducing agent and toning agent. The amount of the azolium salt to be added is not particularly limited, and the amount may preferably be 1×10^{-6} mole to 2 moles, more preferably 1×10^{-3} mole to 0.5 mole, per mole of silver.

【0145】

The thermally processed image recording material may optionally contain a mercapto compound, disulfide compound or thione compound to accelerate, suppress, or control development, or increase efficiency in spectral sensitivity, or to improve storability before and after development. Examples thereof include, for example, those compounds described in JP-A-10-62899, paragraphs 0067 to 0069, compounds of the formula (I) and specific examples thereof mentioned in

JP-A-10-186572, paragraphs 0033 to 0052, those described in EP0803764A1, page 20, lines 36 to 56, those described in Japanese Patent Application No. 11-273670. Among them, mercapto-substituted heteroaromatic compounds are preferred.

【0146】

A toning agent is preferably added to the thermally processed image recording material. Examples of the toning agent are described in JP-A-10-62899, paragraphs 0054 to 0055, EP0803764A1, page 21, lines 23 to 48 and Japanese Patent Application No. 10-213487. Preferred examples include phthalazinones (e.g., phthalazinone, phthalazinone derivatives such as 4-(1-naphthyl)phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone and 2,3-dihydro-1,4-phthalazinone phthalic acids (e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, tetrachlorophthalic anhydride and so forth); phthalazines (e.g., phthalazine, phthalazine derivatives such as 4-(1-naphthyl)phthalazine, 6-isopropylphthalazine, 6-t-butylphthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydrophthalazine and metal salts thereof); combinations of phthalazines and phthalic acids. Particularly preferred examples include the combinations of phthalazines and phthalic acids.

【0147】

Plasticizers and lubricants that can be used for the image-forming layer are described in JP-A-11-65021, paragraph 0117. Ultrahigh contrast agents for forming ultrahigh contrast images and addition methods and amounts therefor are described in the same publication, paragraph 0118, JP-A-11-223898, paragraphs 0136 to 0193, Japanese Patent Application No. 11-87297, compounds of the formula (H), formulas (1) to (3), formulas (A) and (B) and those mentioned in Japanese Patent Application No. 11-91652 as compounds of the formulas (III) to (V) (specific compounds: Chem. 21 to Chem. 24); and hardness enhancement promoters are described in JP-A-11-65021, paragraph 0102, and JP-A-11-223898, paragraphs 0194 to 0195.

【0148】

When formic acid or a formic acid salt is used as a strongly fogging substance, it is preferably used on the side having the image-forming layer containing a photosensitive silver halide in an amount of 5 mmol or less, more preferably 1 mmol or less, per 1 mole of silver.

【0149】

When an ultrahigh contrast agent is used in the thermally processed image

recording material, an acid formed by hydration of diphosphorus pentoxide or a salt thereof is preferably used together with the ultrahigh contrast agent. Examples of the acid formed by hydration of diphosphorus pentoxide or a salt thereof include metaphosphoric acid (salt), pyrophosphoric acid (salt), orthophosphoric acid (salt), triphosphoric acid (salt), tetraphosphoric acid (salt), hexametaphosphoric acid (salt) and so forth. Particularly preferably used acids formed by hydration of diphosphorus pentoxide or salts thereof are orthophosphoric acid (salt) and hexametaphosphoric acid (salt). Specific examples of the salt are sodium orthophosphate, sodium dihydrogenorthophosphate, sodium hexametaphosphate, ammonium hexametaphosphate and so forth. The acid formed by hydration of diphosphorus pentoxide or a salt thereof may be used in a desired amount (coating amount per 1 m² of the thermally processed image recording material) depending on the desired performance including sensitivity and fog. However, it can be used in an amount of preferably 0.1–500 mg/m², more preferably 0.5–100 mg/m².

【0150】

The thermally processed image recording material may be provided with a surface protective layer, for example, to prevent adhesion of the image-forming layer. The surface protective layer may consist of a single layer or a plurality of layers. The surface protective layer is described in, for example, JP-A-11-65021, paragraphs 0119 to 0120. While gelatin is preferred as the binder in the surface protective layer, polyvinyl alcohol (PVA) is also preferably used. As the gelatin, for example, inert gelatin (e.g., Nitta Gelatin 750), phthalized gelatin (e.g., Nitta Gelatin 801) and so forth can be used. Examples of PVA include, for example, completely saponified PVA, PVA-105, partially saponified PVA, PVA-205 and PVA-335, denatured polyvinyl alcohol, MP-203 (all from Kuraray Co., Ltd.) and so forth. The application amount of the polyvinyl alcohol (per m² of the support) for protective layers is preferably 0.3–4.0 g/m², more preferably 0.3–2.0 g/m² (per one layer).

【0151】

When the thermally processed image recording material is used for, in particular, printing use in which dimensional change is critical, polymer latex is preferably used also in a protective layer or a back layer. Such latex is described in “Gosei Jushi Emulsion (Synthetic Resin Emulsion)”, compiled by Taira Okuda and Hiroshi Inagaki, issued by Kobunshi Kanko Kai (1978); “Gosei Latex no Oyo (Application of Synthetic Latex)”, compiled by Takaaki Sugimura, Yasuo Kataoka,

Souichi Suzuki and Keishi Kasahara, issued by Kobunshi Kanko Kai (1993); Soichi Muroi, "Gosei Latex no Kagaku (Chemistry of Synthetic Latex)", Kobunshi Kanko Kai (1970) and so forth. Specific example thereof include latex of methyl methacrylate (33.5 weight %)/ethyl acrylate (50 weight %)/methacrylic acid (16.5 weight %) copolymer, latex of methyl methacrylate (47.5 weight %)/butadiene (47.5 weight %)/itaconic acid (5 weight %) copolymer, latex of ethyl acrylate/methacrylic acid copolymer, latex of methyl methacrylate (58.9 weight %)/2-ethylhexyl acrylate (25.4 weight %)/styrene (8.6 weight %)/2-hydroxyethyl methacrylate (5.1 weight %)/acrylic acid (2.0 weight %) copolymer, latex of methyl methacrylate (64.0 weight %)/styrene (9.0 weight %)/butyl acrylate (20.0 weight %)/2-hydroxyethyl methacrylate (5.0 weight %)/acrylic acid (2.0 weight %) copolymer and so forth. As for the binder of the protective layer, there may be used the combination of polymer latex disclosed in Japanese Patent Application No. 11-6872, and techniques disclosed in Japanese Patent Application No. 11-143058, paragraphs 0021-0025, Japanese Patent Application No. 11-6872, paragraphs 0027-0028, and Japanese Patent Application No. 11-199626, paragraphs 0023-0041. The ratio of the polymer latex in the surface protective layer with respect to the total binder is preferably 10-90 weight%, particularly preferably 20-80 weight %. Coated amount of the total binder (including water-soluble polymer and latex polymer) in the surface protective layer (for one layer) is preferably 0.3-5.0 g/m², more preferably 0.3-2.0 g/m² (per m² of the support).

【00152】

The temperature for preparation of the coating solution for the image-forming layer may preferably be 30°C to 65°C, more preferably 35°C to 60°C, most preferably 35°C to 55°C. The temperature of the coating solution immediately after the addition of the polymer latex may preferably be kept at 30°C to 65°C. A reducing agent and a silver salt of an organic acid may preferably be mixed before the addition of polymer latex.

【0153】

The image-forming layer is provided as one or more layers on the support. When it is provided as a monolayer, the layer contains a silver salt of an organic acid, photosensitive silver halide, reducing agent and binder, and it may contain desired additional materials such as toning agent, coating aid and other auxiliary agents. When the layer is bilayer, the first image-forming layer (in general, the layer adjacent to the support) must contain a silver salt of an organic acid and

photosensitive silver halide, and the second image-forming layer or said two layers must contain the other ingredients. Multicolor photothermographic material may contain these two layers for each color, or may contain all necessary ingredients in a single layer as described in U.S. Patent No. 4,708,928. As for multicolor photosensitive photothermographic materials containing multiple dyes, each emulsion layer is kept individually by using a functional or non-functional barrier layer between the adjacent photosensitive layers as described in U.S. Patent No. 4,460,681.

【0154】

In the image-forming layer, various types of dyes and pigments may be used to improve color tone, to prevent interference fringes generated during laser exposure, and to prevent irradiation (e.g., C.I. Pigment Blue 60, C.I. Pigment Blue 64, C.I. Pigment Blue 15:6). These techniques are detailed in International Patent Publication WO98/36322, JP-A-10-268465, JP-A-11-338098 and so forth.

【0155】

In the thermally processed image recording material, an antihalation layer may be provided in a distant position from a light source relative to the image-forming layer.

【0156】

Thermally processed image recording materials generally have non-photosensitive layers in addition to the photosensitive layer. Depending on their positions, the non-photosensitive layers are classified into (1) a protective layer to be provided on a photosensitive layer (the opposite side of the support); (2) an intermediate layer to be provided between two or more of photosensitive layers or between a photosensitive layer and a protective layer; (3) an undercoat layer to be provided between a photosensitive layer and a support; (4) a back layer to be provided on a side opposite to the photosensitive layer. The filter layer is provided in the thermally processed image recording material as the layer (1) or (2). The antihalation layer is provided in the thermally processed image recording material as the layer (3) or (4).

【0157】

The antihalation layer is described in JP-A-11-65021, paragraphs 0123 to 0124, JP-A-11-223898, JP-A-9-230531, JP-A-10-36695, JP-A-10-104779, JP-A-11-231457, JP-A-11-352625, JP-A-11-352626 etc. The antihalation layer contains an antihalation dye that shows absorption for the light exposure

wavelength. When the light exposure wavelength is in the infrared region, an infrared absorption dye can be used, and in such a case, it is preferable to use a dye that does not show absorption for the visible region. When the antihalation is attained by using a dye that shows absorption for the visible region, it is preferably used in such a manner that color of the dye should not substantially remain after the image formation. To this end, means for enabling decoloration by the heat of heat development is preferably used, and it is particularly preferable to add a thermodecoloring dye and a base precursor to a non-photosensitive layer so that the layer should function as an antihalation layer. These techniques are disclosed in JP-A-11-231457 and so forth.

【0158】

The amount of the decoloring dye may be determined depending on purpose of the dye. In general, the dye is used in an amount to give an optical density (absorbance) of larger than 0.1 measured at an intended wavelength. The optical density is preferably 0.2 to 2. The amount of the dye to give such optical density may be generally from about 0.001 to about 1 g/m².

【0159】

Decoloring of dyes in that manner can lower optical density of the material after the thermal development to 0.1 or less. Two or more different decoloring dyes may be used in the thermodecoloring type recording materials or thermally processed image recording materials. Similarly, two or more different base precursors may be used in combination. In such thermal decoloration utilizing a decoloring dye and base precursor, it is preferable to use together a substance that decreases the melting point by 3° C (deg) or more when it is mixed with a base precursor, such as those described in JP-A-11-352626 (e.g., diphenylsulfone, 4-chlorophenyl-(phenyl)sulfone) in view of thermodecoloration property etc.

【0160】

A colorant that shows absorption maximum in the range of 300-450 nm may be added in order to improve change of silver color tone and images with time. Such a colorant is described in JP-A-62-210458, JP-A-63-104046, JP-A-63-103235, JP-A-63-208846, JP-A-63-306436, JP-A-63-314535, JP-A-01-61745, Japanese Patent Application No. 11-276751 and so forth. Such a colorant is usually added in an amount of 0.1 mg/m² to 1 g/m², and it is preferably added to a back layer, which is provided on the side opposite to the side

on which the image-forming layer is provided.

【0161】

The thermally processed image recording material is preferably a so-called single-sided photosensitive material comprising at least one image-forming layer containing a silver halide emulsion on one side of support, and a back layer on the other side.

【0162】

The thermally processed image recording material may preferably contain a matting agent for improving the transferability of the material. Matting agents are described in JP-A-11-65021, paragraphs 0126 to 0127. The matting agent is preferably added in an amount of 1-400 mg/m², more preferably 5 to 300 mg/m², as the amount per 1 m² of the thermally processed image recording material. While the matting degree of the surface of the emulsion layer is not particularly limited so long as the material is free from stardust defects, Beck's smoothness of the surface is preferably 30 seconds to 2000 seconds, more preferably 40 seconds to 1500 seconds. Beck smoothness can be easily determined according to Japanese Industrial Standard (JIS) P8119, "Test Method for Smoothness of Paper and Paperboard by Beck Test Device" and TAPPI Standard Method T479.

【0163】

The matting degree of the back layer preferably falls 10 seconds to 1200 seconds, more preferably 20 seconds to 800 seconds, further preferably 40 seconds to 500 seconds in terms of the Beck's smoothness.

【0164】

The matting agent may preferably be incorporated in the outermost surface layer of the thermally processed image recording material or a layer which functions as the outermost surface layer, or alternatively, in a layer close to the outer surface or a layer which acts as a so-called protective layer.

【0165】

The back layers that are applicable to the thermally processed image recording material are described in JP-A-11-65021, paragraphs 0128 to 0130.

【0166】

The thermally processed image recording material preferably has a film surface pH of 6.0 or less, more preferably 5.5 or less before heat development. While the lower limit is not particularly defined, it is normally around 3. For controlling the film surface pH, an organic acid such as phthalic acid derivatives or

a nonvolatile acid such as sulfuric acid, and a volatile base such as ammonia are preferably used to lower the film surface pH. In particular, ammonia is preferred to achieve a low film surface pH, because it is highly volatile and therefore it can be removed before coating or heat development. A method for measuring the film surface pH is described in Japanese Patent Application No. 11-87297, paragraph 0123.

【0167】

A hardening agent may be used in the image-forming layer, the protective layer, the back layer and other layers. Examples of the hardening agent are described in T.H. James, "THE THEORY OF THE PHOTOGRAPHIC PROCESS, FOURTH EDITION", Macmillan Publishing Co., Inc., 1977, pp. 77-87. There may be preferably used chromium alum, 2,4-dichloro-6-hydroxy-s-triazine sodium salt, N,N-ethylenebis(vinylsulfonacetamide), N,N-propylene-bis(vinylsulfonacetamide), as well as the polyvalent metal ions described on page 78 of the above article, polyisocyanates described in U.S. Patent No. 4,281,060 and JP-A-6-208193; epoxy compounds described in U.S. Patent No. 4,791,042; vinylsulfone compounds described in JP-A-62-89048 and so forth.

【0168】

The hardening agent is added to coating solutions as a solution. Preferred addition time of the solution to the coating solution of the protective layer resides in a period of from 180 minutes before the coating to just before the coating, preferably 60 minutes to 10 seconds before the coating. The method and conditions for mixing are not particularly limited, so long as the effects of the invention are fully exhibited. Specific examples of the mixing method include a method in which a mixing is performed in a tank designed so as to obtain a desired average residence time which is calculated from addition flow rate and feeding amount to a coater, a method utilizing a static mixer described in N. Harnby, M.F. Edwards, A.W. Nienow, "Ekitai Kongo Gijutsu (Techniques for Mixing Liquids)", translated by Koji Takahashi, Chapter 8, Nikkan Kogyo Shinbunsha, 1989 and so forth.

【0169】

Surfactants that can be used in the thermally processed image recording material are described in JP-A-11-65021, paragraph 0132; usable solvents are described in the above patent document in paragraph 0133; usable supports are described in the above patent document in paragraph 0134; usable antistatic and electroconductive layers are described in the above patent document in paragraph

0135; and usable methods for forming color images are described in the above patent document in paragraph 0136; lubricants are described in JP-A-11-84573, paragraphs 0061-0064 and Japanese Patent Application No. 11-106881, paragraphs 0049-0062.

【0170】

Preferably used as a transparent support is a polyester film, in particular, polyethylene terephthalate film, subjected to a heat treatment in a temperature range of 130-185° C in order to relax the internal distortion formed in the film during the biaxial stretching so that thermal shrinkage distortion occurring during the heat development should be eliminated. When the thermally processed image recording material is for medical use, the transparent support may be colored with blue dyes (e.g., with Dye-1 described in Examples of JP-A-8-240877), or may be colorless. For the support, techniques for undercoating described in JP-A-11-84574 (utilizing water-soluble polyester), JP-A-10-186565 (utilizing styrene/butadiene copolymer), JP-A-11-106881, paragraphs 0063-0080 (utilizing vinylidene chloride copolymer) and so forth are preferably used. As for antistatic layers and undercoating, techniques disclosed in JP-A-56-143430, JP-A-56-143431, JP-A-58-62646, JP-A-56-120519, JP-A-11-84573, paragraphs 0040-0051, U.S. Patent No. 5,575,957, JP-A-11-223898, paragraphs 0078-0084 and so forth can also be used.

【0171】

The thermally processed image recording material is preferably a monosheet type material (the monosheet uses no additional sheet as required by image receiving materials, and can form images directly on the thermally processed image recording material itself).

【0172】

The thermally processed image recording material may further contain an antioxidant, a stabilizer, a plasticizer, an ultraviolet absorber or a coating aid. Such additives may be added to any of photosensitive layers or non-photosensitive layers. For these additives, WO98/36322, EP803764A1, JP-A-10-186567, JP-A-10-18568 and so forth may be referred to.

【0173】

The coating method for the preparation of the thermally processed image recording material is not particularly limited, and any coating methods may be employed. Specific examples thereof include various types of coating techniques,

for example, extrusion coating, slide coating, curtain coating, dip coating, knife coating, flow coating, extrusion coating utilizing a hopper of the type described in U.S. Patent No. 2,681,294 and so forth. Among them, preferred examples include extrusion coating and slide coating described in Stephen F. Kistler, Petert M. Schweizer, "LIQUID FILM COATING", published by CHAPMAN & HALL Co., Ltd., 1997, pp.399-536, and a most preferable example includes the slide coating. An example of the shape of a slide coater used for the slide coating is shown in Figure 11b, 1, on page 427 of the aforementioned reference. If desired, two or more layers may be formed at the same time, for example, according to the methods described from page 399 to page 536 of the aforementioned reference, or the methods described in U.S. Patent No. 2,761,791 and British Patent No. 837,095.

【0174】

The coating solution for the image-forming layer is preferably a so-called thixotropic flow. Thixotropy means a property of fluid that viscosity of fluid lowers with increase of shear rate. While any apparatus may be used for measurement of viscosity, for example, RFS Fluid Spectrometer from Rheometrics Far East Co., Ltd. is preferably used and the measurement is performed at 25°C. Viscosity of the coating solution for a layer containing the silver salt of the organic acid is preferably 400 mPa·s to 100,000 mPa·s, more preferably 500 mPa·s to 20,000 mPa·s, at a shear rate of 0.1 sec⁻¹. The viscosity is preferably 1 mPa·s to 200 mPa·s, more preferably 5 mPa·s to 80 mPa·s, at a shear rate of 1000 sec⁻¹.

【0175】

Various systems exhibiting thixotropic property are known and, for example, described in "Koza Rheology (Lecture on Rheology)", Kobunshi Kanko Kai; Muroi & Morino, "Kobunshi Latex (Polymer Latex)", Kobunshi Knako Kai and so forth. A fluid is required to contain a large amount of fine solid microparticles to exhibit thixotropic property. For enhancing thixotropic property, it is effective that the fluids is added with a viscosity-increasing linear polymer, or fine solid microparticles to be contained have anisotropic shapes and an increased aspect ratio. Use of an alkaline viscosity-increas-

ing agent or a surfactant is also effective for that purpose.

【0176】

Other techniques that can be used for the production of the thermally processed image recording material are also described in EP803764A1, EP883022A1, WO98/36322, JP-A-56-62648, JP-A-58-62744, JP-A-9-281637,

JP-A-9-297367, JP-A-9-304869, JP-A-9-311405, JP-A-9-329865,
 JP-A-10-10669, JP-A-10-62899, JP-A-10-69023, JP-A-10-186568,
 JP-A-10-90823, JP-A-10-171063, JP-A-10-186565, JP-A-10-186567,
 JP-A-10-186569, JP-A-10-186570, JP-A-10-186571, JP-A-10-186572,
 JP-A-10-197974, JP-A-10-197982, JP-A-10-197983, JP-A-10-197985,
 JP-A-10-197986, JP-A-10-197987, JP-A-10-207001, JP-A-10-207004,
 JP-A-10-221807, JP-A-10-282601, JP-A-10-288823, JP-A-10-288824,
 JP-A-10-307365, JP-A-10-312038, JP-A-10-339934, JP-A-11-7100,
 JP-A-11-15105, JP-A-11-24200, JP-A-11-24201, JP-A-11-30832,
 JP-A-11-84574, JP-A-11-65021, JP-A-11-109547, JP-A-11-125880,
 JP-A-11-129629, JP-A-11-133536, JP-A-11-133537, JP-A-11-133538,
 JP-A-11-133539, JP-A-11-133542, JP-A-11-133543, JP-A-11-223898 and
 JP-A-11-352627.

【0177】

The thermally processed image recording material may be developed in any manner. Usually, an imagewise exposed thermally processed image recording material is developed by heating. The temperature for the development is preferably 80° C to 250°C, more preferably 100°C to 140°C. The development time is preferably 1–180 seconds, more preferably 10–90 seconds, particularly preferably 10–40 seconds.

【0178】

For thermal development for the material, preferred is a plate heater system. For heat development by the plate heater system, the method described in JP-A-11-133572 is preferred. The plate heater system described in this references is a heat development apparatus wherein a thermally processed image recording material on which a latent image is formed is brought into contact with a heating means in a heat development section to obtain a visible image. In this apparatus, the heating means comprises a plate heater, and a plurality of presser rollers are disposed facing to one surface of the plate heater. Heat development of the thermally processed image recording material is attained by passing the material between the presser rollers and the plate heater. The plate heater is preferably sectioned into 2 to 6 stages, and the temperature of the top stage is preferably kept lower by 1 to 10°C or so than that of the others. Such a method is also described in JP-A-54-30032. Such a plate heater system can remove moisture and organic solvent contained in the thermally processed image recording

material out of the material, and prevent deformation of the support of the thermally processed image recording material due to rapid heating of the material.

【0179】

The thermally processed image recording material of the present invention can be exposed in any manner. As light source of exposure, laser rays are preferred. As the laser, gas lasers (Ar⁺, He-Ne), YAG lasers, dye lasers, semiconductor lasers and so forth are preferred. A combination of semiconductor laser and second harmonic generating device may also be used. Preferred are gas or semiconductor lasers for red to infrared emission.

【0180】

As an example of a medical laser imager provided with a light exposure section and a heat development section, Fuji Medical Dry Laser Imager FM-DP L can be mentioned. FM-DP L is explained in Fuji Medical Review, No. 8, pages 39-55, and those techniques can of course be used in laser imagers for the thermally processed image recording material. Further, it can be used as a thermally processed image recording material for laser imagers in "AD network", which was proposed by Fuji Medical System as a network system that conforms to the DICOM standard.

【0181】

The thermally processed image recording material forms a monochromatic image based on silver image, and is preferably used as a thermally processed image recording material for use in medical diagnosis, industrial photography, printing and COM.

【0182】

【Examples】

The present invention will be specifically explained with reference to the following examples. The materials, amounts, ratios, types of treatments, procedures of treatments and so forth shown in the following examples can be optionally changed so long as such change does not depart from the spirit of the present invention. Therefore, the configuration of the present invention is not limited to the following examples.

【0183】

<Example 1>

<<Preparation of Organic acid silver salt dispersion A>>

Organic acid silver salt dispersion A was prepared by using such a large

scale crystallization facility as shown in Fig. 8. That is, to a tank 22, 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 L of distilled water and 120 L of tert-butanol were added. To the mixture, 49.2 L of 5 mol/L aqueous solution of NaOH was added at 75° over 5 minutes with stirring, and allowed to react for 60 minutes to obtain a solution of sodium behenate. On the other hand, 206.2 L of an aqueous solution containing 40.4 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 21. Further, 600 L of pure water was measured in the tank 35, and circulated via the pumps 31 and 32 through the pipeline mixers 33 and 34 (Model PM-10 produced by Mizuho Kogyo Co., Ltd.) at a flow rate of 50 L/minute for each route. While stirring was performed by operating the pipeline mixers at 3,600 rpm, the aqueous solution of silver nitrate was added at a constant flow rate of 1.45 L/minute to each route by using the pumps 23 and 24, and after 5 seconds, addition of the aqueous solution of sodium behenate was started at a constant flow rate of 4.9 L/minute to each route by using the pumps 25 and 26, so that the solutions were stored in the tank 35. Cooling water at 10° C was supplied to a jacket of the tank 35 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 (S/cm. The solid content obtained as described above was stored as a wet cake without being dried.

【0184】

Distilled water and polyvinyl alcohol were added to the obtained wet cake of organic acid silver according to the composition mentioned below, and centrifuged by using T. K. Homodisper Model 2M-5 (Tokushu Kika Kogyo Co., Ltd.) at 5,000 rpm for 15 minute to obtain a crude dispersion.

Composition of crude dispersion:

Distilled water	42.4 kg
Organic acid silver salt (wet cake having solid content of 40%)	56 kg
Polyvinyl alcohol (PVA-205, Kuraray Co., Ltd.)	2.2 kg

The obtained crude dispersion was dispersed once by using Microfluidizer

(M110S-EH, using G10Z interaction chamber produced by Mizuho Kogyo Co., Ltd.) at a pressure of 1600 kg/cm² to obtain Organic acid silver salt dispersion A. In this operation, the inlet temperature immediately before the dispersion and the outlet temperature immediately after the dispersion were controlled to be 5° C and 30° C, respectively.

【0185】

<<Preparation of Organic acid silver salt dispersion B>>

Organic acid silver salt dispersion B was prepared in such a large scale crystallization facility as shown in Fig. 8 by using only one addition and mixing line among the two of such lines in the facility. That is, to the tank 12, 43.8 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 211.5 L of distilled water and 60 L of tert-butanol were added. To the mixture, 24.6 L of 5 mol/L aqueous solution of NaOH was added at 75° C over 5 minutes with stirring, and allowed to react at for 60 minutes to obtain a solution of sodium behenate. On the other hand, 103.1 L of an aqueous solution containing 20.2 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 21. Further, 300 L of pure water was measured in the tank 35, and circulated via the pump131 through the pipeline mixer 33 (Model PM-10 produced by Mizuho Kogyo Co., Ltd.) at a flow rate of 50 L/minute. While stirring was performed by operating the pipeline mixer at 3,600 rpm, the aqueous solution of silver nitrate was added at a constant flow rate of 1.45 L/minute by using the pump 23, and after 5 seconds, addition of the aqueous solution of sodium behenate was started at a constant flow rate of 4.9 L/minute by using the pump 25, so that the solutions were stored in the tank 35. Cooling water at 10° C was supplied to a jacket of the tank 135 at a flow rate of 100 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 (S/cm. The solid content obtained as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion A to obtain Organic acid silver salt dispersion B.

【0186】

<<Preparation of Organic acid silver salt grain dispersion C>>

Organic acid silver salt dispersion C was prepared by using such a large

scale crystallization facility as shown in Fig. 3. That is, to the tank 112, 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 L of distilled water and 120 L of tert-butanol were added. To the mixture, 49.2 L of 5 mol/L aqueous solution of NaOH was added at 75° C over 5 minutes with stirring, and allowed to react for 60 minutes to obtain a solution of sodium behenate. On the other hand, 206.2 L of an aqueous solution containing 40.4 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 11. Further, 600 L of pure water was measured in the tank 20, and circulated via the pump 17 through the pipeline mixer 18 (Model PM-20 produced by Mizuho Kogyo Co., Ltd.) at a flow rate of 100 L/minute. While stirring was performed by operating the pipeline mixer at 2,400 rpm, the aqueous solution of silver nitrate was added at a constant flow rate of 2.9 L/minute by using the pump 15, and after 5 seconds, addition of the aqueous solution of sodium behenate was started at a constant flow rate of 9.8 L/minute to by using the pump 16, so that the solutions were stored in the tank 20. Cooling water at 10° C was supplied to a jacket of the tank 20 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 (S/cm. The solid content obtained as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion A to obtain Organic acid silver salt dispersion C.

【0187】

<<Preparation of Organic acid silver salt grain dispersion D>>

Organic acid silver salt dispersion DD was prepared by using such a large scale crystallization facility as shown in Fig. 3. That is, to the tank 12, 43.8 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 211.5 L of distilled water and 60 L of tert-butanol were added. To the mixture, 24.6 L of 5 mol/L aqueous solution of NaOH was added at 75° C over 5 minutes with stirring, and allowed to react at for 60 minutes to obtain a solution of sodium behenate. On the other hand, 103.1 L of an aqueous solution containing 20.2 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 111. Further, 300 L of pure water was measured in the tank 20, and circulated via the pump 17 through the pipeline mixer 18 (Model PM-20 produced by Mizuho Kogyo Co., Ltd.) at a flow

rate of 100 L/minute. While stirring was performed by operating the pipeline mixer at 2,400 rpm, the aqueous solution of silver nitrate was added at a constant flow rate of 2.9 L/minute by using the pump 15, and after 2.5 seconds, addition of the aqueous solution of sodium behenate was started at a constant flow rate of 9.8 L/minute by using the pump 116, so that the solutions were stored in the tank 20. Cooling water at 10° C was supplied to a jacket of the tank 20 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 μ S/cm. The solid content obtained as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion A to obtain Organic acid silver salt dispersion D.

【0188】

<<Preparation of Organic acid silver salt dispersion E>>

Organic acid silver salt dispersion E was prepared by using such a large scale crystallization facility as shown in Fig. 13. That is, to the tank 112, 43.8 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 221.5 L of distilled water and 60 L of tert-butanol were added. To the mixture, 24.6 L of 5 mol/L aqueous solution of NaOH was added at 75° C over 5 minutes with stirring, and allowed to react for 60 minutes to obtain a solution of sodium behenate. On the other hand, 103.1 L of an aqueous solution containing 20.2 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 11. Further, 300 L of pure water was measured in the tank 20, and circulated via the pump 117 through the pipeline mixer 18 (Model PM-20 produced by Mizuho Kogyo Co., Ltd.) at a flow rate of 50 L/minute. While stirring was performed by operating the pipeline mixer at 1,600 rpm, the aqueous solution of silver nitrate was added at a constant flow rate of 1.45 L/minute by using the pump 15, and after 5 seconds, addition of the aqueous solution of sodium behenate was started at a constant flow rate of 4.9 L/minute to by using the pump 16, so that the solutions were stored in the tank 120. Cooling water at 10° C was supplied to a jacket of the tank 20 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by

suction filtration and washed with water until electric conductivity of the filtrate became 30 $\mu\text{S}/\text{cm}$. The solid content obtained as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion A to obtain Organic acid silver salt dispersion E.

【0189】

Physical properties including grain size, viscosity and so forth of Organic acid silver salt dispersions A to E obtained as described above and increase of filtration pressure during their preparation are shown in Table 1. In this example, grain size was measured by using a laser diffraction type particle size measurement apparatus (SALD-200J, Shimadzu Corp.). The viscosity was measured at 25° C by using RFS fluid spectrometer produced by Rheometric Far East Co., Ltd. Further, increase of filtration pressure was measured as a difference of final pressure and initial pressure in filtration of 2 kg of each dispersion using Epocel Filter EC having a diameter of 1.5 cm (produced by Pall Corp.) at a flow rate of 50 ml/minute.

【0190】

【Table 1】

Dispersion	Grain size		Viscosity (mPA.s)	Increase of filtration pressure (kg/cm ²)	Photographic performance		Fog increase ratio
	Average (μm)	Variation coefficient (%)			Dmin	Sensitivity	
A (Invention)	0.38	16	19	0.18	100	105	1.1
B (Invention)	0.38	17	19	0.18	100	105	1.1
C (Invention)	0.39	16	19	0.18	100	105	1.1
D (Invention)	0.43	18	18	0.21	102	101	1.4
E (Invention)	0.37	16	21	0.19	101	106	1.2

【0191】

<<Preparation of Organic acid silver salt dispersion F>>

In an amount of 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 L of distilled water and 120 L of tert-butanol stirred at 75° C in a reaction tank were added with 49.2 L of 5 mol/L aqueous solution of NaOH over 5 minutes, and allowed to react for 60 minutes to obtain a solution of sodium behenate. Separately, 206.2 L of an aqueous solution containing 40.4 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C. A reaction vessel containing 635 L of distilled water and 30 L of tert-butanol was maintained at 30° C, and added with the whole volume of the aqueous silver nitrate solution with stirring at a constant flow rate. After 7 minutes, it was started to add the whole volume of the sodium behenate solution at a constant flow rate. The addition times of the aqueous silver nitrate solution and the sodium behenate solution in this operation were 60 minutes and 62 minute, respectively. Therefore, during the last 9 minutes, only the sodium behenate solution was added. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 μ S/cm. The solid content obtained as described above was stored as a wet cake without being dried.

【0192】

Distilled water and polyvinyl alcohol were added to the obtained wet cake according to the composition mentioned below, and treated by using T. K. Homodisper Model 2M-5 (Tokushu Kika Kogyo Co., Ltd.) at 5,000 rpm for 15 minute to obtain a crude dispersion. The obtained grains had a mean grain size of 5.36 μ m.

Composition of crude dispersion:

Distilled water	42.4 kg
Organic acid silver salt (wet cake having solid content of 40%)	56 kg
Polyvinyl alcohol (PVA-205, Kuraray Co., Ltd.)	2.2 kg

The obtained crude dispersion was treated once by using Microfluidizer (M110S-EH, using G10Z interaction chamber produced by Mizuho Kogyo Co., Ltd.) at a pressure of 1600 kg/cm² to obtain Organic acid silver salt grain dispersion F.

In this operation, the inlet temperature immediately before the dispersion and the outlet temperature immediately after the dispersion were controlled to be 5° C and 30° C, respectively. The obtained dispersion showed a mean grain size and viscosity of 0.62 μm and 18 mPa·s, respectively, as shown in Table 2.

【0193】

<<Preparation of Organic acid silver salt dispersion G>>

Organic acid silver salt dispersion G was prepared in such a large scale crystallization facility as shown in Fig. 3 by using the addition section and mixing unit shown in Fig. 4 as the pipeline mixer 18. That is, to the tank 12, 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 L of distilled water and 120 L of tert-butanol were added. To the mixture, 49.2 L of 5 mol/L aqueous solution of NaOH was added at 75° C over 5 minutes with stirring, and allowed to react for 60 minutes to obtain a solution of sodium behenate. On the other hand, 206.2 L of an aqueous solution containing 40.4 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 11. Further, 600 L of pure water was measured in the tank 20, and circulated via the pump 17 through the pipeline mixer 18 (Model PM-20 produced by Mizuho Kogyo Co., Ltd., Fig. 4) from a reaction field solution addition inlet C' shown in Fig. 4 at a flow rate of 100 L/minute. While stirring was performed by operating the pipeline mixer at 2,400 rpm, the aqueous solution of silver nitrate was added from a silver ion-containing solution addition inlet A' shown in Fig. 4 at a constant flow rate of 2.9 L/minute, and after 5 seconds, addition of the aqueous solution of sodium behenate was started from an organic acid alkali metal salt solution addition inlet B' shown in Fig. 4 at a constant flow rate of 9.8 L/minute, so that the solutions were stored in the tank 0 via the heat exchanger 19. Cooling water at 10° C was supplied to the heat exchanger and a jacket of the tank 20 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 $\mu\text{S}/\text{cm}$. The solid content obtained as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion F to obtain Organic acid silver salt dispersion G.

【0194】

<<Preparation of Organic acid silver salt dispersion H>>

Organic acid silver salt dispersion H was prepared in such a large scale crystallization facility as shown in Fig. 3 by using the addition section and mixing unit shown in Fig. 5 (a) as the pipeline mixer 18. That is, to the tank 12, 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 L of distilled water and 120 L of tert-butanol were added. To the mixture, 49.2 L of 5 mol/L aqueous solution of NaOH was added at 75° C over 5 minutes with stirring, and allowed to react for 60 minutes to obtain a solution of sodium behenate. On the other hand, 206.2 L of an aqueous solution containing 40.4 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 11. Further, 600 L of pure water was measured in the tank 20, and circulated via the pump 17 through the pipeline mixer 18 (Model PM-20 produced by Mizuho Kogyo Co., Ltd., Fig. 5 (a)) from a reaction field solution addition inlet C' (inner diameter: 56.5 mm) shown in Fig. 5 (a) at a flow rate of 100 L/minute. While stirring was performed by operating the pipeline mixer at 2,400 rpm (corresponding to a peripheral speed of 13 m/minute), the aqueous solution of silver nitrate was added from a silver ion-containing solution addition inlet A' (inner diameter: 10 mm) shown in Fig. 5 (a) at a constant flow rate of 2.9 L/minute, and after 5 seconds, addition of the aqueous solution of sodium behenate was started from an organic acid alkali metal salt solution addition inlet B' (inner diameter: 13.3 mm) shown in Fig. 5 (a) at a constant flow rate of 9.8 L/minute, so that the solutions were stored in the tank 20 via a heat exchanger 19. The distance between the silver ion-containing solution addition inlet A' and the organic acid alkali metal salt solution addition inlet B' was adjusted to 400 mm. Cooling water at 10° C was supplied to the heat exchanger and a jacket of the tank 20 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 μ S/cm. The solid content obtained as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion F to obtain Organic acid silver salt dispersion H.

【0195】

<<Preparation of Organic acid silver salt dispersion I>>

Organic acid silver salt dispersion I was prepared in such a large scale crystallization facility as shown in Fig. 3 by using the addition section and mixing

unit shown in Fig. 5 (b) as the pipeline mixer 18. That is, to the tank 11, 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 L of distilled water and 120 L of tert-butanol were added. To the mixture, 49.2 L of 5 mol/L aqueous solution of NaOH was added at 75° C over 5 minutes with stirring, and allowed to react for 60 minutes to obtain a solution of sodium behenate. On the other hand, 206.2 L of an aqueous solution containing 404 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 12. Further, 600 L of pure water was measured in the tank 20, and circulated via the pump 17 through the pipeline mixer 18 (Model PM-20 produced by Mizuho Kogyo Co., Ltd., Fig. 8 (b)) from a reaction field solution addition inlet C' (inner diameter: 56.5 mm) shown in Fig. 5 (b) at a flow rate of 100 L/minute. While stirring was performed by operating the pipeline mixer at 2,400 rpm, addition of the aqueous solution of sodium behenate was started from an organic acid alkali metal salt solution addition inlet B' (inner diameter: 13.3 mm) shown in Fig. 5 (b) at a constant flow rate of 9.8 L/minute, and after 5 seconds, the aqueous solution of silver nitrate was added from a silver ion-containing solution addition inlet A' (inner diameter: 10 mm) shown in Fig. 5 (b) at a constant flow rate of 2.9 L/minute, so that the solutions were stored in the tank 120 via the heat exchanger 19. The distance between the organic acid silver alkali metal salt solution addition inlet B' and the silver ion-containing solution addition inlet A' was adjusted to 400 mm. Cooling water at 10° C was supplied to the heat exchanger and a jacket of the tank 20 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 μ S/cm. The solid content obtained as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion F to obtain Organic acid silver salt dispersion I.

[0196]

<<Preparation of Organic acid silver salt dispersion J>>

Organic acid silver salt dispersion J was prepared in such a large scale crystallization facility as shown in Fig. 4 by using the addition section and mixing unit shown in Fig. 6 as the pipeline mixer 18. That is, to the tank 12, 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 L of

distilled water and 120 L of tert-butanol were added. To the mixture, 49.2 L of 5 mol/L aqueous solution of NaOH was added at 75° C over 5 minutes with stirring, and allowed to react for 60 minutes to obtain a solution of sodium behenate. On the other hand, 206.2 L of an aqueous solution containing 40.4 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 11. Further, 600 L of pure water was measured in the tank 20, and circulated via the pump 17 through the pipeline mixer 18 (Model PM-20 produced by Mizuho Kogyo Co., Ltd., Fig. 6) from a reaction field solution addition inlet C' (inner diameter: 150 mm) shown in Fig. 6 at a flow rate of 100 L/minute. While stirring was performed by operating the pipeline mixer at 2,400 rpm, the aqueous solution of silver nitrate was added from a silver ion-containing solution addition inlet A' (inner diameter: 10 mm) shown in Fig. 6 at a constant flow rate of 2.9 L/minute, and after 5 seconds, addition of the aqueous solution of sodium behenate was started from an organic acid alkali metal salt solution addition inlet B' (inner diameter: 13.3 mm) shown in Fig. 6 at a constant flow rate of 9.8 L/minute, so that the solutions were stored in the tank 20 via the heat exchanger 19. The distance between the silver ion-containing solution addition inlet A' and the organic acid alkali metal salt solution addition inlet B' was adjusted to 400 mm. Cooling water at 10° C was supplied to the heat exchanger and a jacket of the tank 20 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 μ S/cm. The solid content obtained as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion F to obtain Organic acid silver salt dispersion J.

【0197】

<<Preparation of Organic acid silver salt dispersion K>>

Organic acid silver salt dispersion K was prepared in such a large scale crystallization facility as shown in Fig. 3 by using the addition section and mixing unit shown in Fig. 6 as the pipeline mixer 18. That is, to the tank 12, 876 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 4230 L of distilled water and 1200 L of tert-butanol were added. To the mixture, 49.2 L of 5 mol/L aqueous solution of NaOH was added with stirring at 75° C over 5 minutes, and allowed to react for 60 minutes to obtain a solution of sodium

behenate. On the other hand, 2062 L of an aqueous solution containing 404 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 11. Further, 600 L of pure water was measured in the tank 20, and circulated via the pump 17 through the pipeline mixer 18 (Model LR-1 produced by Mizuho Kogyo Co., Ltd., Fig. 6) from a reaction field solution addition inlet C' (inner diameter: 13.3 mm) shown in Fig. 6 at a flow rate of 1000 mL/minute. While stirring was performed by operating the pipeline mixer at 10,000 rpm (corresponding to a peripheral speed of 13 m/minute), the aqueous solution of silver nitrate was added from a silver ion-containing solution addition inlet A' (inner diameter: 5 mm) shown in Fig. 6 at a constant flow rate of 29 mL/minute, and after 5 seconds, addition of the aqueous solution of sodium behenate was started from an organic acid alkali metal salt solution addition inlet B' (inner diameter: 5 mm) shown in Fig. 6 at a constant flow rate of 98 mL/minute, so that the solutions were stored in the tank 20 via the heat exchanger 19. The distance between the silver ion-containing solution addition inlet A' and the organic acid alkali metal salt solution addition inlet B' was adjusted to 100 mm. Cooling water at 10° C was supplied to the heat exchanger and a jacket of the tank 20 at a flow rate of 20 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 μ S/cm. The solid content obtained as described above was stored as a wet cake without being dried.

【0198】

Distilled water and polyvinyl alcohol were added to the obtained wet cake according to the composition mentioned below, and treated by using T. K. Homodisper Model 2M-5 (Tokushu Kika Kogyo Co., Ltd.) at 5,000 rpm for 15 minute to obtain a crude dispersion.

Composition of crude dispersion:

Distilled water	424 g
Organic acid silver salt (wet cake having solid content of 40%)	560 g
Polyvinyl alcohol (PVA-205, Kuraray Co., Ltd.)	22 g

The obtained crude dispersion was treated once by using Microfluidizer

(M110S-EH, using G10Z interaction chamber produced by Mizuho Kogyo Co., Ltd.) with a pressure of 1600 kg/cm² to obtain Organic acid silver salt dispersion K. In this operation, the inlet temperature immediately before the dispersion and the outlet temperature immediately after the dispersion were controlled to be 5° C and 30° C, respectively.

The obtained grains had a mean grain size of 5.36 μm.

【0199】

<<Preparation of Organic acid silver salt dispersion L>>

Organic acid silver salt dispersion L was prepared in such a large scale crystallization facility as shown in Fig. 3 by using the addition section and mixing unit shown in Fig. 6 as the pipeline mixer 118. That is, to the tank 12, 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 L of distilled water and 120 L of tert-butanol were added. To the mixture, 49.2 L of 5 mol/L aqueous solution of NaOH was added with stirring at 75° C over 5 minutes, and allowed to react for 60 minutes to obtain a solution of sodium behenate. On the other hand, 206.2 L of an aqueous solution containing 40.4 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 11. Further, 600 L of pure water was measured in the tank 120, and circulated via the pump 17 through the pipeline mixer 18 (Model PM-20 produced by Mizuho Kogyo Co., Ltd., Fig. 6) from a reaction field solution addition inlet C' (inner diameter: 56.5 mm) shown in Fig. 6 at a flow rate of 100 L/minute. While stirring was performed by operating the pipeline mixer at 2,400 rpm, the aqueous solution of silver nitrate was added from a silver ion-containing solution addition inlet A' (inner diameter: 10 mm) shown in Fig. 6 at a constant flow rate of 2.9 L/minute, and after 5 seconds, addition of the aqueous solution of sodium behenate was started from an organic acid alkali metal salt solution addition inlet B' (inner diameter: 13.3 mm) shown in Fig. 6 at a constant flow rate of 9.8 L/minute, so that the solutions were stored in the tank 20 via a heat exchanger 19. The distance between the silver ion-containing solution addition inlet A' and the organic acid alkali metal salt solution addition inlet B' was adjusted to 400 mm. Cooling water at 10° C was supplied to the heat exchanger and a jacket of the tank 20 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 (S/cm). The solid content obtained

as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion F to obtain Organic acid silver salt dispersion L.

【0200】

<<Preparation of Organic acid silver salt dispersion M>>

Organic acid silver salt dispersion M was prepared in such a large scale crystallization facility as shown in Fig. 3 by using the addition section and mixing unit shown in Fig. 7 as the pipeline mixer 118. That is, to the tank 112, 87.6 kg of behenic acid (Edenor C22-85R, trade name, manufactured by Henkel Co.), 423 L of distilled water and 120 L of tert-butanol were added. To the mixture, 49.2 L of 5 mol/L aqueous solution of NaOH was added at 75° C over 5 minutes with stirring, and allowed to react for 60 minutes to obtain a solution of sodium behenate. On the other hand, 206.2 L of an aqueous solution containing 40.4 kg of silver nitrate (pH 4.0) was prepared and kept at 10°C in the tank 11. Further, 600 L of pure water was measured in the tank 20, and circulated via the pump 17 through the pipeline mixer 18 (Model PM-20 produced by Mizuho Kogyo Co., Ltd., Fig. 7) from a reaction field solution addition inlet C' shown in Fig. 7 at a flow rate of 100 L/minute. While stirring was performed by operating the pipeline mixer at 2,400 rpm, the aqueous solution of silver nitrate was added from a silver ion-containing solution addition inlet A' shown in Fig. 7 at a constant flow rate of 2.9 L/minute, and after 5 seconds, addition of the aqueous solution of sodium behenate was started from an organic acid alkali metal salt solution addition inlet B' shown in Fig. 7 at a constant flow rate of 9.8 L/minute, so that the solutions were stored in the tank 20 via a heat exchanger 19. Cooling water at 10° C was supplied to the heat exchanger and a jacket of the tank 20 at a flow rate of 200 L/minute, and as a result, the average temperature in the tank was measured to be 30° C. The mixture was left with stirring for 20 minutes as it was to lower the temperature to 25° C. Then, the solid content was separated by suction filtration and washed with water until electric conductivity of the filtrate became 30 (S/cm. The solid content obtained as described above was stored as a wet cake without being dried. Thereafter, dispersion operation was performed in the same manner as that for Organic acid silver salt dispersion F to obtain Organic acid silver salt dispersion M. Physical properties including grain size, viscosity and so forth of Organic acid silver salt dispersions F to M obtained as described above and increase of filtration pressure during their preparation are shown in Table 2. Measurements are the

same as in the organic acid silver salt dispersions A to E.

【0201】

【Table 2】

Dispersion	Grain size		Viscosity (mPa.s)	Increase of filtration pressure (kg/cm ²)	Photographic performance		Fog increase ratio
	Average (μm)	Variation coefficient (%)			Dmin	Sensitivity	
F (Comparative)	0.62	28	18	0.23	100	100	1.5
G (Comparative)	0.55	24	19	0.22	100	103	1.3
H (Invention)	0.41	16	18	0.18	101	105	1.1
I (Comparative)	0.89	31	22	0.27	100	101	1.4
J (Invention)	0.39	16	19	0.18	101	105	1.1
K (Invention)	0.59	26	19	0.22	100	101	1.3
L (Invention)	0.37	16	20	0.18	100	105	1.1
M (Invention)	0.32	16	23	0.10	100	105	1.0

【0202】

<Comparative Experiment>

As a comparative experiment, it was attempted to prepare a dispersion in such a large scale crystallization facility as shown in Fig. 3 by using the addition section and mixing unit shown in Fig. 6 as the pipeline mixer 18. In this experiment, when it was attempted to add a silver nitrate aqueous solution at a constant flow rate of 2.9 L/minute from the silver ion-containing solution addition inlet A' of Fig. 6 having an inner diameter of 5 mm, pressure inside the pipeline exceeded the capacity of the pump, and hence addition at the desired flow rate could not be realized. The Reynolds number at this time was about 22,000. Therefore, improvement of the facility itself, for example, increase of pressure limit of pump used for feeding liquids, is required in order to obtain a Reynolds number exceeding 20,000. However, it is not practical.

【0203】

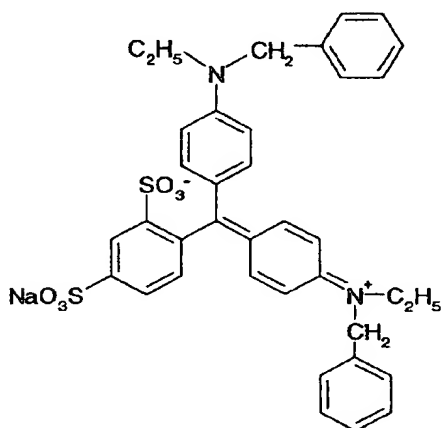
<Example 2>

The structures of compounds used for the production of thermally processed image recording materials in this examples are shown below.

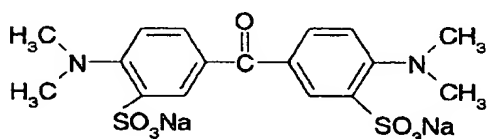
【0204】

【Chemical formula 15】

Blue dye compound 14



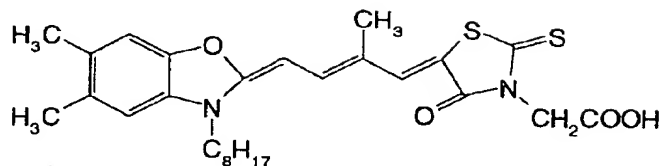
Yellow dye compound 15



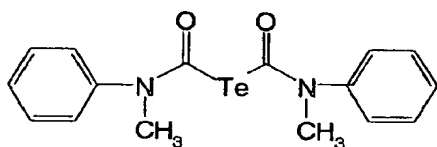
【0205】

【Chemical formula 16】

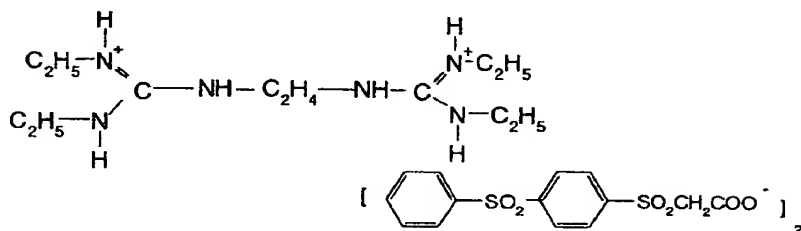
Spectral sensitizing dye A



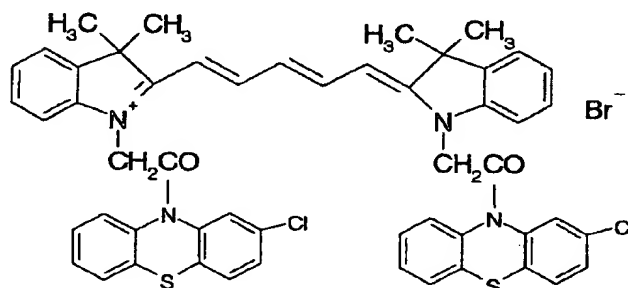
Tellurium sensitizer B



Base precursor compound 11



Cyanine dye compound 13



【0206】

<<Preparation of undercoated PET support>>

(Preparation of PET support)

Using terephthalic acid and ethylene glycol, polyethylene terephthalate having an intrinsic viscosity of 0.66 (measured in phenol/tetrachloroethane = 6/4 (weight ratio) at 25°C) was obtained in a conventional manner. This was pelletized, and the pellets were dried at 130°C for 4 hours, melted at 300°C, extruded from a

T-die, and quenched to prepare an unstretched film having such a thickness that the film thickness after thermal fixation should become 175 μm . The film was stretched along the longitudinal direction by 3.3 times at 110°C using rollers having different peripheral speeds and then stretched along the transverse direction at 130°C by 4.5 times using a tenter. Thereafter, the film was subjected to thermal fixation at 240°C for 20 seconds and relaxed by 4% along the transverse direction at the same temperature. Then, after chucks of the tenter were released, the both edges of the film were knurled, and the film was rolled up at 4 kg/cm^2 to provide a roll of the film having a thickness of 175 μm .

【0207】

(Surface corona discharging treatment)

Using a solid state corona discharging treatment machine Model 6KVA manufactured by Piller Inc., both surfaces of the support were treated at room temperature at 20 m/minute. In this case, from the read out values of the electric current and voltage, it was seen that the treatment of 0.375 $\text{kV}\cdot\text{A}\cdot\text{minute}/\text{m}^2$ was applied to the support. The treated frequency in this case was 9.6 kHz and the gap clearance between the electrode and the dielectric roll was 1.6 mm.

【0208】

(Preparation of undercoated support)

(1) Preparation of coating solutions for undercoat layers

Formulation 1 (for undercoat layer on photosensitive layer side)

Pesresin A-515GB made by Takamatsu

Yushi K.K. (30 weight % solution)	234 g
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Polyethylene glycol monononylphenyl

ether (mean ethylene oxide number = 8.5, 10 weight % solution)	21.5 g
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MP-1000 made by Soken Kagaku K.K.

(polymer microparticles, mean particle size: 0.4 μm)	0.91 g
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Distilled water	744 ml
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【0209】

Formulation 2 (for first layer on back surface)

Styrene-butadiene copolymer latex

(solid content: 40weight %, weight ratio

of styrene/butadiene = 68/32)	158 g
2,4-Dichloro-6-hydroxy-S-triazine sodium salt (8 weight % aqueous solution)	20 g
1 weight % Aqueous solution of sodium laurylbenzenesulfonate	10 ml
Distilled water	854 ml

【0210】

Formulation 3 (for second layer on back surface side)

SnO ₂ /SbO (weight ratio: 9/1, mean particle size: 0.038 μm, 17 weight % dispersion)	84 g
Gelatin (10% aqueous solution)	89.2 g
Metorose TC-5 made by Shin-Etsu Chemical Co., Ltd. (2% aqueous solution)	8.6 g
MP-1000 (polymer microparticles) made by Soken Kagaku K.K.	0.01 g
1 weight % Aqueous solution of sodium dodecylbenzenesulfonate	10 ml
NaOH (1%)	6 ml
Proxel (made by ICI Co.)	1 ml
Distilled water	805 ml

【0211】

(Preparation of undercoated support)

After applying the aforementioned corona discharging treatment to both surfaces of the aforementioned biaxially stretched polyethylene terephthalate support having a thickness of 175 μm, one surface (photosensitive layer side) thereof was coated with the undercoating solution of Formulation 1 by a wire bar in a wet coating amount of 6.6 ml/m² (per one surface) and dried at 180°C for 5 minutes. Then, the back surface thereof was coated with the undercoating solution of Formulation 2 by a wire bar in a wet coating amount of 5.7 ml/m² and dried at 180°C for 5 minutes. The back surface thus coated was further coated with the undercoating solution of Formulation 3 by a wire bar in a wet coating amount of 7.7 ml/m² and dried at 180°C for 6 minutes to prepare an undercoated support.

【0212】

<<Preparation of coating solution for back surface>>

(Preparation of Solid microparticle dispersion (a) of base precursor)

In an amount of 64 g of Base precursor compound 11, 28 g of diphenylsulfone and 10 g of a surface active agent, Demor N (manufactured by Kao Corporation), were mixed with 220 ml of distilled water, and the mixture was beads-dispersed using a sand mill (1/4 Gallon Sand Grinder Mill, manufactured by Imex Co.) to obtain Solid microparticle dispersion (a) of the base precursor compound having a mean particle size of 0.2 μ m.

【0213】

(Preparation of dye solid microparticle dispersion)

In an amount of 9.6 g of Cyanine dye compound 13 and 5.8 g of sodium p-dodecylbenzenesulfonate were mixed with 305 ml of distilled water and the mixture was beads-dispersed using a sand mill (1/4 Gallon Sand Grinder Mill, manufactured by Imex Co.) to obtain a dye solid microparticle dispersion having a mean particle size of 0.2 μ m.

【0214】

(Preparation of coating solution for antihalation layer)

In an amount of 17 g of gelatin, 9.6 g of polyacrylamide, 70 g of the aforementioned Solid microparticle dispersion (a) of the base precursor, 56 g of the aforementioned dye solid microparticle dispersion, 1.5 g of monodispersed polymethyl methacrylate microparticles (mean particle size: 8 μ m, standard deviation of particle size: 0.4), 0.03 g of benzoisothiazolinone, 2.2 g of sodium polyethylenesulfonate, 0.2 g of Blue dye compound 14, 3.9g of Yellow dye compound 15 and 844 ml of water were mixed to prepare a coating solution for antihalation layer.

【0215】

(Preparation of coating solution for back surface protective layer)

In a container kept at 40°C, 50 g of gelatin, 0.2 g of sodium polystyrenesulfonate, 2.4 g of N,N-ethylenebis(vinylsulfonacetamide), 1 g of sodium t-octylphenoxyethoxyethanesulfonate, 30 mg of benzoisothiazolinone, 37 mg of N-perfluorooctylsulfonyl-N-propylalanine potassium salt, 0.15 g of polyethylene glycol mono(N-perfluorooctylsulfonyl-N-propyl2-aminoethyl) ether [average polymerization degree of ethylene oxide: 15], 32 mg of $C_8F_{17}SO_3K$, 64 mg of $C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_4(CH_2)_4-SO_3Na$, 8.8 g of an acrylic acid/ethyl acrylate copolymer (copolymerization ratio (weight ratio): 5/95), 0.6 g of Aerosol OT (manufactured by American Cyanamid Company), 1.8 g (as liquid paraffin) of a liquid

paraffin emulsion and 950 ml of water were mixed to form a coating solution for back surface protective layer.

【0216】

<<Preparation of Silver halide emulsion 1>>

In an amount of 1421 ml of distilled water was added with 3.1 ml of 1 weight % potassium bromide solution, and further added with 3.5 ml of 0.5 mol/L sulfuric acid and 31.7 g of phthalized gelatin. Separately, Solution A was prepared by adding distilled water to 22.22 g of silver nitrate to dilute it to 95.4 ml, and Solution B was prepared by diluting 15.9 g of potassium bromide with distilled water to a volume of 97.4 ml. To the aforementioned mixture maintained at 34° C and stirred in a stainless steel reaction vessel, the whole volume of Solution A and Solution B was added over 45 seconds at constant flow rates. Then, the mixture was added with 10 ml of 3.5 weight % aqueous hydrogen peroxide solution, and further added with 10.8 ml of a 10 weight % aqueous solution of benzimidazole. Further, Solution C was prepared by adding distilled water to 51.86 g of silver nitrate to dilute it to 317.5 ml, and Solution D was prepared by diluting 45.8 g of potassium bromide with distilled water to a volume of 400 ml. The whole volume of Solution C was added to the mixture over 20 minutes at a constant flow rate. Solution D was added by the control double jet method while pAg was maintained at 8.1. Hexachloroiridic acid (III) potassium salt in an amount of 1×10^{-4} mole per mole of silver was added at one time 10 minutes after the addition of Solutions C and D was started. Further, an aqueous solution of potassium iron(II) hexacyanide in an amount of 3×10^{-4} mole per mole of silver was added at one time 5 seconds after the addition of Solution C was completed. Then, the mixture was adjusted to pH 3.8 using 0.5 mol/L sulfuric acid, and the stirring was stopped. Then, the mixture was subjected to precipitation, desalting and washing with water, adjusted to pH 5.9 with 1 mol/L sodium hydroxide to form a silver halide dispersion having pAg of 8.0.

【0217】

The aforementioned silver halide dispersion was added with 5 ml of a 0.34 weight % methanol solution of 1,2-benzisothiazolin-3-one with stirring at 38° C, and after 40 minutes since then, added with a methanol solution of Spectral sensitizing dye A in an amount of 1×10^{-3} mole per mole of silver. After 1 minutes, the mixture was warmed to 47°C, and 20 minutes after the warming, added with 7.6×10^{-5} mole of sodium benzenethiosulfonate per mole of silver as a methanol

solution. Further after 5 minutes, the mixture was added with Tellurium sensitizer B as a methanol solution in an amount of 1.9×10^{-4} mole per mole of silver followed by ripening for 91 minutes. The mixture was added with 1.3 ml of a 0.8 weight % methanol solution of N,N'-dihydroxy-N"-diethylmelamine, and 4 minutes later, added with 3.7×10^{-3} mole per mole of silver of 5-methyl-2-mercaptobenzimidazole and 4.9×10^{-3} mole per mole of silver of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole as a methanol solution to prepare Silver halide emulsion 1. The grains in the prepared silver halide emulsion were pure silver bromide grains having a mean diameter as spheres of 0.046 μm and a variation coefficient of 20% for mean diameter as spheres. The grain size and others were obtained from averages for 1000 grains by using an electron microscope. The [100] face ratio of these grains was determined to be 80% by the Kubelka-Munk method.

【0218】

<<Preparation of Silver halide emulsion 2>>

Silver halide emulsion 2 was prepared in the same manner as the preparation of Silver halide emulsion 1 except that the liquid temperature upon grain formation was changed from 34°C to 49°C, addition time of Solution C was changed to 30 minutes and potassium iron(II) hexacyanide was not used. Then, as in the case of Silver halide emulsion 1, the steps of precipitation, desalting, washing with water and dispersion were performed. Furthermore, in the same manner as in the case of Silver halide emulsion 1 except that the addition amount of Spectral sensitizing dye A was changed to 7.5×10^{-4} mole per mole of silver, the addition amount of Tellurium sensitizer B was changed to 1.1×10^{-4} mole per mole of silver, and the addition amount of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole was changed to 3.3×10^{-3} mole of per mole of silver, spectral sensitization, chemical sensitization, and addition of 5-methyl-2-mercaptobenzimidazole and 1-phenyl-2-heptyl-5-mercapto-1,3,4-traizole were performed to obtain Silver halide emulsion 2. Emulsion grains of Silver halide emulsion 2 were pure silver bromide cubic grains having a mean grain diameter of 0.080 μm as spheres and a variation coefficient of 20% for diameter as spheres.

【0219】

<<Preparation of Silver halide emulsion 3>>

Silver halide emulsion 3 was prepared in the same manner as the preparation of Silver halide emulsion 1 except that the liquid temperature upon

grain formation was changed from 34°C to 27°C. Further, as in the case of Silver halide emulsion 1, the steps of precipitation, desalting, washing with water and dispersion were performed. Then, Silver halide emulsion 3 was obtained in the same manner as in the case of Silver halide emulsion 1 except that the addition amount of Spectral sensitizing dye A solid dispersion (gelatin aqueous solution) was changed to 6×10^{-3} mole per mole of silver and the addition amount of Tellurium sensitizer B was changed to 5.2×10^{-4} mole per mole of silver. Emulsion grains of Silver halide emulsion 3 were pure silver bromide cubic grains having a mean grain diameter of $0.038 \mu\text{m}$ as spheres and a variation coefficient of 20% for diameter as spheres.

【0220】

<<Preparation of Mixed emulsion A for coating solution>>

In an amount of 70% by weight of Silver halide emulsion 1, 15% by weight of Silver halide emulsion 2 and 15% by weight of Silver halide emulsion 3 were mixed and added with benzothiazolium iodide in an amount of 7×10^{-3} mole per mole of silver as a 1 weight % aqueous solution.

【0221】

<<Preparation of 25 weight % dispersion of reducing agent complex>>

In an amount of 10 kg of 1:1 complex of 2,2-methylenebis-(4-ethyl-6-tert-butylphenol) and triphenylphosphine oxide, and 10 kg of a 20 weight % aqueous solution of denatured polyvinyl alcohol (Poval MP203, manufactured by Kuraray Co., Ltd.) were added with 16 kg of water, and mixed sufficiently to form slurry. The slurry was fed by a diaphragm pump to a sand mill of horizontal type (UVM-2, manufactured by Imex Co.) containing zirconia beads having a mean diameter of 0.5 mm, and dispersed for 3 hours and 30 minutes. Then, the slurry was added with 0.2 g of benzothiazolinone sodium salt and water so that the concentration of the reducing agent should become 25 weight % to obtain a solid microparticle dispersion of reducing agent complex. The reducing agent complex particles contained in the dispersion of reducing agent complex obtained as described above had a median diameter of $0.46 \mu\text{m}$ and the maximum particle size of $2.0 \mu\text{m}$ or less. The obtained reducing agent complex dispersion was filtered through a polypropylene filter having a pore size of $10.0 \mu\text{m}$ to remove dusts and so forth, and stored.

【0222】

<<Preparation of 10 weight % dispersion of mercapto compound>>

In an amount of 5 kg of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole and 5 kg of a 20 weight % aqueous solution of denatured polyvinyl alcohol (Poval MP203, manufactured by Kuraray Co., Ltd.) were added with 8.3 kg of water, and mixed sufficiently to form slurry. The slurry was fed by a diaphragm pump to a sand mill of horizontal type (UVM-2, manufactured by Imex Co.) containing zirconia beads having a mean diameter of 0.5 mm, and dispersed for 6 hours. Then, the slurry was added with water so that the concentration of the mercapto compound should become 10 weight % to obtain a mercapto compound dispersion. The mercapto compound particles contained in the mercapto compound dispersion obtained as described above had a median diameter of 0.40 μm and the maximum particle size of 2.0 μm or less. The obtained mercapto compound dispersion was filtered through a polypropylene filter having a pore size of 10.0 μm to remove dusts and so forth, and stored. The dispersion was filtered again through a polypropylene filter having a pore size of 10.0 μm immediately before use.

【0223】

<<Preparation of 26 weight % dispersion of Organic polyhalogenated compound :1>>

In an amount of 5 kg of tribromomethylphenylsulfone, 5 kg of a 20 weight % aqueous solution of denatured polyvinyl alcohol (Poval MP203, manufactured by Kuraray Co., Ltd.) and 213 g of 20 weight % aqueous solution of sodium triisopropyl naphthalenesulfonate were added with 10 kg of water, and mixed sufficiently to form slurry. The slurry was fed by a diaphragm pump to a sand mill of horizontal type (UVM-2, manufactured by Imex Co.) containing zirconia beads having a mean diameter of 0.5 mm, and dispersed for 5 hours. Then, the slurry was added with 0.2 g of benzisothiazolinone sodium salt and water so that the concentration of the organic polyhalogenated compound should become 26 weight % to obtain an organic polyhalogenated compound dispersion. The organic polyhalogenated compound particles contained in the polyhalogenated compound dispersion obtained as described above had a median diameter of 0.41 μm and the maximum particle size of 2.0 μm or less. The obtained organic polyhalogenated compound dispersion was filtered through a polypropylene filter having a pore size of 3.0 μm to remove dusts and so forth, and stored. Then, the dispersion was stored at 10° C or lower until use.

【0224】

<<Preparation of 25 weight % dispersion of Organic polyhalogenated compound :2>>

In an amount of 5 kg of tribromomethyl-3-pentanoylaminophenylsulfone, 2.5

kg of 20 weight % aqueous solution of denatured polyvinyl alcohol (Poval MP203, manufactured by Kuraray Co., Ltd.), 213 g of 20 weight % aqueous solution of sodium triisopropyl naphthalenesulfonate and 10 kg of water were mixed sufficiently to form slurry. The slurry was fed by a diaphragm pump to a sand mill of horizontal type (UVM-2, manufactured by Imex Co.) containing zirconia beads having a mean particle size of 0.5 mm, and dispersed for 5 hours. Then, the slurry was added with 0.2 g of benzisothiazolinone sodium salt and water so that the concentration of the organic polyhalogenated compound should become 25 weight % to obtain organic polyhalogenated compound dispersion. The organic polyhalogenated compound particles contained in the organic polyhalogenated compound dispersion obtained as described above had a median particle size of 0.41 μ m and the maximum particle size of 2.0 μ m or less. The obtained organic polyhalogenated compound dispersion was filtered through a polypropylene filter having a pore size of 3.0 μ m to remove dusts and so forth, and stored.

【0225】

<<Preparation of 5 weight % solution of phthalazine compound>>

In an amount of 8 kg of denatured polyvinyl alcohol (MP-203, manufactured by Kuraray Co., Ltd.) was dissolved in 174.57 kg of water and then added with 3.15 kg of 20 weight % aqueous solution of sodium triisopropyl naphthalenesulfonate and 14.28 kg of 70 weight % aqueous solution of 6-isopropylphthalazine to obtain a 5 weight % solution of 6-isopropylphthalazine.

【0226】

<<Preparation of 20 weight % dispersion of pigment>>

In an amount of 64 g of C.I. Pigment Blue 60, 6.4 g of Demor N manufactured by Kao Corporation and 250 g of water were mixed sufficiently to provide slurry. Then, 800 g of zirconia beads having a mean particle size of 0.5 mm were placed in a vessel together with the slurry and the slurry was dispersed by a dispersing machine (1/4G Sand Grinder Mill; manufactured by Imex Co.) for 25 hours to obtain a pigment dispersion. The pigment particles contained in the dispersion obtained as described above had a mean particle size of 0.21 μ m.

【0227】

<<Preparation of 40 weight % SBR latex>>

SBR latex purified by ultrafiltration (UF) was obtained as follows.

The SBR latex mentioned below diluted by 10 times with distilled water was diluted and purified by using an UF-purification module FS03-FC-FUYO3A1

(manufactured by Daisen Membrane System K.K.) until the ion conductivity became 1.5 mS/cm, and added with Sandet-BL (manufactured by SANYO CHEMICAL INDUSTRIES, LTD.) to a concentration of 0.22 weight %. Further, the latex was added with NaOH and NH₄OH so that the ratio of Na⁺ ion:NH₄⁺ ion should become 1:2.3 (molar ratio) to adjust pH to 8.4. At this point, the concentration of the latex was 40 weight %.

(SBR latex: a latex of -St(71)-Bu(26)-AA(3)-)

The latex had the following characteristics: mean particle size of 0.1 μm, concentration of 45%, equilibrated moisture content of 0.6 weight % at 25°C and 60% RH, and ion conductivity of 4.2 mS/cm (measured for the latex stock solution (40%) at 25°C by using a conductometer, CM-30S, manufactured by Toa Electronics, Ltd.), pH 8.2.

【0228】

<<Preparation of coating solution for image-forming layer>>

In an amount of 103 g of organic acid silver salt dispersion prepared in Example 1, 1.1 g of the 20 weight % aqueous dispersion of pigment, 5 g of 20 weight % of aqueous solution of polyvinyl alcohol PVA-205 (Kuraray Co., Ltd.), 26 g of the 25 weight % dispersion of the reducing agent complex, 8.2 g in total of the dispersions of Organic polyhalogenated compounds : 1 and 2 (weight ratio = 1:3), 6.2 g of the 10 weight % dispersion of mercapto compound, 106 g of the 40 weight % aqueous solution of SBR latex (Tg: 24° C) undergone the ultrafiltration (UF) purification and pH adjustment and 18 ml of the 5 weight % solution of phthalazine compound were combined, and mixed sufficiently with 10 g of Silver halide mixed emulsion A immediately before coating to prepare a coating solution for image-forming layer (photosensitive layer, emulsion layer). The coating solution was fed as it was to a coating die in such a feeding amount giving a coating amount of 70 ml/m² and coated. The viscosity of the obtained coating solution for image-forming layer was measured by a B-type viscometer manufactured by Tokyo Keiki K.K. and found to be 85 [mPa·s] at 40°C (Rotor No. 1, 60 rpm). The viscosity of the coating solution was measured at 25° C by RFS fluid spectrometer produced by Rheometric Far East Co., Ltd., and found to be 1500, 220, 70, 40 and 20 [mPa·s] at shear rates of 0.1, 1, 10, 100 and 1000 [1/second], respectively.

【0229】

<<Preparation of coating solution for intermediate layer on image-forming layer side>>

In an amount of 772 g of a 10 weight % aqueous solution of polyvinyl alcohol, PVA-205 (manufactured by Kuraray Co., Ltd.), 5.3 g of the 20 weight % dispersion of pigment, 226 g of 27.5 weight % solution of methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio (by weight): 64/9/20/5/2) latex, 2 ml of 5 weight % aqueous solution of Aerosol OT (manufactured by American Cyanamid Company), 10.5 ml of 20 weight % aqueous solution of phthalic acid diammonium salt and water in such an amount giving a total amount of 880 g were mixed and adjusted to pH 7.5 with NaOH to form a coating solution for intermediate layer. This coating solution was fed to a coating die in such an amount that gave a coating amount of 10 ml/m². The viscosity of the coating solution measured by a B-type viscometer at 40°C (Rotor No. 1, 60 rpm) was 21 [mPa·s].

【0230】

<<Preparation of coating solution for 1st protective layer on image-forming layer side>>

An amount of 64 g of inert gelatin was dissolved in water, which was added with 80 g of 27.5 weight % latex solution of methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio (by weight): 64/9/20/5/2), 23 ml of 10 weight % methanol solution of phthalic acid, 23 ml of 10 weight % aqueous solution of 4-methylphthalic acid, 28 ml of 0.5 mol/L sulfuric acid, 5 ml of 5 weight % aqueous solution of Aerosol OT (manufactured by American Cyanamid Company), 0.5 g of phenoxyethanol, 0.1 g of benzoisothiazolinone, and water in such an amount that gave a total amount of 750 g to form a coating solution. The coating solution was mixed with 26 ml of 4 weight % chromium alum by a static mixer immediately before coating, and fed to a coating die in such an amount that gave a coating amount of 18.6 ml/m². The viscosity of the coating solution measured by a B-type viscometer (Rotor No. 1, 60 rpm) at 40°C was 17 [mPa·s].

【0231】

<<Preparation of coating solution for 2nd protective layer on image-forming layer side>>

An amount of 80 g of inert gelatin was dissolved in water, which was added with 102 g of 27.5 weight % latex solution of methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio (by weight): 64/9/20/5/2), 3.2 ml of 5 weight % solution of

N-perfluorooctylsulfonyl-N-propylalanine potassium salt, 32 ml of 2 weight % aqueous solution of polyethylene glycol mono(N-perfluorooctylsulfonyl-N-propyl-2-aminoethyl) ether [average polymerization degree of ethylene oxide = 15], 23 ml of 5 weight % aqueous solution of Aerosol OT (manufactured by American Cyanamid Company), 4 g of polymethyl methacrylate microparticles (mean particle size: 0.7 μm), 21 g of polymethyl methacrylate microparticles (mean particle size: 4.5 μm), 1.6 g of 4-methylphthalic acid, 4.8 g of phthalic acid, 44 ml of 0.5 mol/L sulfuric acid, 10 mg of benzoisothiazolinone and water in such an amount that gave a total amount of 650 g were mixed to form a coating solution. The coating solution was further mixed with 445 ml of an aqueous solution containing 4 weight % of chromium alum and 0.67 weight % of phthalic acid by a static mixer immediately before coating to form a coating solution for protective layer, and fed to a coating die in such an amount that gave a coating amount of 8.3 ml/m². The viscosity of the coating solution measured by a B-type viscometer (Rotor No. 1, 60 rpm) at 40°C was 9 [mPa·s].

【0232】

<<Preparation of thermally processed image forming material>>

On the back surface side of the aforementioned support having undercoat layers, the coating solution for antihalation layer and the coating solution for back surface protective layer were simultaneously applied as stacked layers so that the applied solid content of the solid microparticle dye in the antihalation layer should be 0.04 g/m², and the applied amount of gelatin in the back surface protective layer should be 1.7 g/m², and dried to form a back layer. Then, on the side opposite to the back side, an image-forming layer (coated silver amount of the silver halide was 0.14 g/m²), intermediate layer, first protective layer and second protective layer were simultaneously coated in this order from the undercoat layer by the slide bead coating method as stacked layers to form a sample of thermally processed image recording material. The conditions of coating and drying were as follows. The coating was performed at a speed of 160 m/min. The gap between the tip of coating die and the support was set to be 0.10 to 0.30 mm, and the pressure in the reduced pressure chamber was adjusted to be lower than the atmospheric pressure by 196–882 Pa. Electrostatic charge of the support was eliminated by ionized wind before the coating.

In the subsequent chilling zone, the coating solutions were cooled with air blow showing a dry-bulb temperature of 10–20° C. Then, the material was

transported without contact, and dried with drying air showing a dry-bulb temperature of 23–45° C and a wet-bulb temperature of 15–21° C in a coil-shaped non-contact type drier. After the drying, the material was conditioned for its moisture content at 25° C and relative humidity of 40–60%, and heated so that the temperature of film surface should become 70–90° C. After the heating, the material was cooled to 25° C as a temperature of film surface. The prepared thermally processed image recording material showed matting degree of 550 seconds for the photosensitive layer side, and 130 seconds for the back surface, in terms of Beck's smoothness. The film surface pH on the photosensitive layer side was measured to be 6.0.

【0233】

<<Evaluation of photographic performance>>

Each thermally processed image recording material was light-exposed and heat-developed (at about 120° C) by using Fuji Medical Dry Laser Imager FM-DP L (equipped with a semiconductor laser of 660 nm and maximum output of 60 mW (IIIB)), and the obtained image was evaluated by a densitometer. The obtained result was evaluated as D_{min} and sensitivity which was a reciprocal of exposure that gave a density higher than D_{min} by 1.0. The sensitivity and the D_{min} were represented with a relative value based on the value of the thermally processed image recording material A, which was taken as 100. Higher sensitivity and lower D_{min} mean higher image reproducing ability of the thermally processed image recording materials. Results are shown in Tables 1 and 2.

【0234】

<<Evaluation of storability after forced time lapse>>

Each thermally processed image recording material was cut into a piece of 30.5 cm x 25.4 cm, of which corners were cut into round corners having a radius of 0.5 cm, and left under conditions of 25° C and relative humidity of 50% for 1 days. Then, 10 sheets of each thermally processed image recording material were sealed into a bag made of a moisture-proof material, and the bag was left for 5 days in an oven at 50° C or a refrigerator at 4° C. Light exposure and heat development were performed in the same manner as in the evaluation of photographic performance, and density and D_{min} of unexposed area were used as values representing fog.

Fog increase ratio = $\frac{[(\text{Fog of sample subjected to high temperature storage}) - (\text{Fog of sample subjected to low temperature storage})]}{(\text{Fog of sample subjected to low temperature storage})}$

of sample subjected to low temperature storage))/[(Maximum concentration of sample subjected to low temperature storage) - (Fog of sample subjected to low temperature storage)]] x 100

A lower fog increase ratio indicates better storability after time lapse. Results are shown in Tables 1 and 2. When two of addition and mixing lines are used in the same scale, a dispersion of equivalent grain size and photographic performance compared with Dispersion C can be prepared by using a flow rate of 1/2 order for each line and a smaller mixing vessel and controlling rotation number as shown in Dispersion A.

【0235】

<<Comparison between the prior art>>

As compared with the dispersion F according to the prior art in which the reaction liquid was added to and stirred and mixed in the open tank, the dispersions H, J, L and M according to the preparing method of the present invention in which the reaction liquid was added to and stirred and mixed in the sealed mixer had totally smaller mean particle sizes, which may be due to no entraining of bubbles into the liquid and low-temperature chargeability. Further, since the atmosphere in which the reaction liquid was added was strictly controlled, there were obtained excellent effects that the grains were more uniformly formed to improve the photographic activity and increase the sensitivity. This can decrease the coated amount of the organic acid silver and realize silver-saving formulation and designing.

【0236】

<<Influence of addition prior to silver ion-containing liquid>>

As compared with the dispersion H according to the preparing method of the present invention, the dispersion I in which the solution of the organic acid alkali salt was added prior to the silver ions clearly had the larger mean particle size and increased fog. The dispersion G in which the simultaneous addition was made had clearly had the larger mean particle size and increased fog.

【0237】

<<Influence of Reynolds number at the time of addition of silver ions>>

When comparison is made among the dispersion J in which the Reynolds number at the time of addition of the silver ion-containing solution was set at about 1100, the dispersion K in which the Reynolds number at the time of addition

of the silver ion-containing solution was lowered to about 220 and the dispersion L in which the Reynolds number was set at about 11000 by decreasing the diameter of the addition pipeline, the dispersions J and L having their Reynolds numbers within the preferable range (500–20000) had smaller mean particle sizes and smaller fogs of the thermally processed image recording materials as compared with the dispersion K having the Reynolds number falling outside the above range. Therefore, it was confirmed that more preferable results could be obtained when the Reynolds number at the time of the addition of the silver ion-containing solution was set in the range of 500–20000.

【0238】

【Effects of the Invention】

According to the present invention, the organic acid silver dispersions having excellent dispersion stability and coating properties are obtained. When such a dispersion is used for a thermally processed image recording material, the thermally processed image recording material having high sensitivity and stability of the image after the thermal development can be obtained. According to the preparing method of the present invention, since mixing can be vigorously performed without entraining of air, the dispersion of the organic acid silver salt can be stably produced.

【Brief Description of the Invention】

【Fig. 1】 A schematic view showing a method for the preparation of organic acid silver salts according to the present invention.

【Fig. 2】 A schematic view showing another method for the preparation of organic acid silver salts according to the present invention.

【Fig. 3】 A schematic view showing one embodiment of the method for the preparation of the organic acid silver salts according to the present invention.

【Fig. 4】 An enlarged view of a mixing section in the one embodiment of the method for the preparation of organic acid silver salts according to the present invention.

【Fig. 5】 An enlarged view of another mixing section in the one embodiment of the method for the preparation of organic acid silver salts according to the present invention.

【Fig. 6】 An enlarged view of a further mixing section in the one embodiment of the method for the preparation of organic acid silver salts according to the present invention.

【Fig. 7】 An enlarged view of a further mixing section in the one embodiment of the

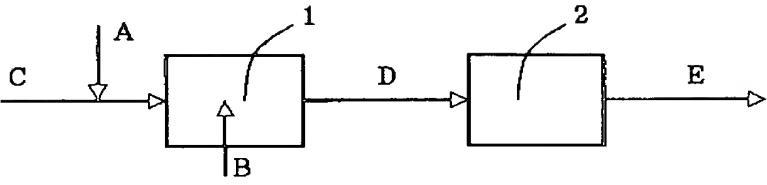
method for the preparation of organic acid silver salts according to the present invention.

【Fig. 8】 A schematic view showing another embodiment of the method for the preparation of the organic acid silver salts according to the present invention.

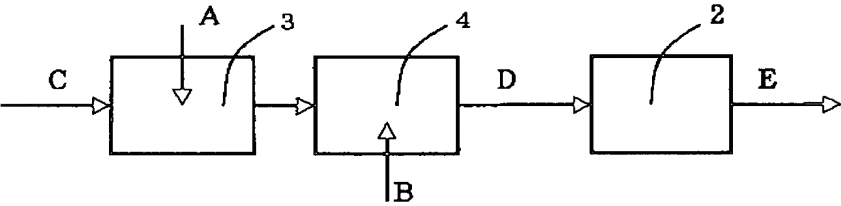
【Explanation of codes】

- 1 sealed mixer
- 2 sealed mixer
- 3 sealed mixer
- 4 sealed mixer
- A pipeline for supplying silver ion-containing solution
- B pipeline for supplying organic acid alkali metal salt solution
- C pipeline for supplying reaction field solution
- E pipeline for discharging organic acid silver salt solution
- 11, 12 tank
- 13, 14 flow meter
- 15-17 pump
- 18 mixer (pipeline mixer)
- 19 heat exchanger
- 20 tank
- 21, 22 tank
- 23-26 pump
- 27-30 flow meter
- 31, 32 pump
- 33, 34 mixer (pipeline mixer)
- 35 pump

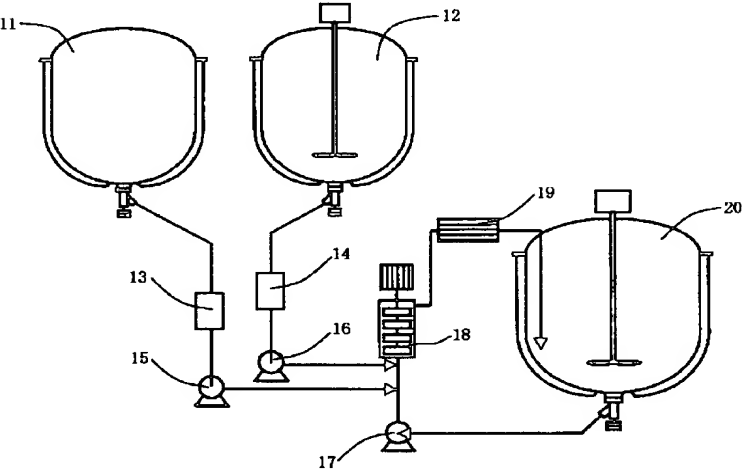
【Fig.1】



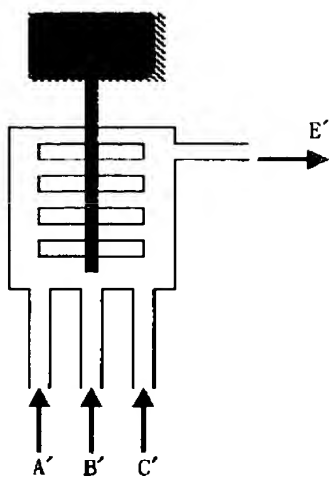
【Fig.2】



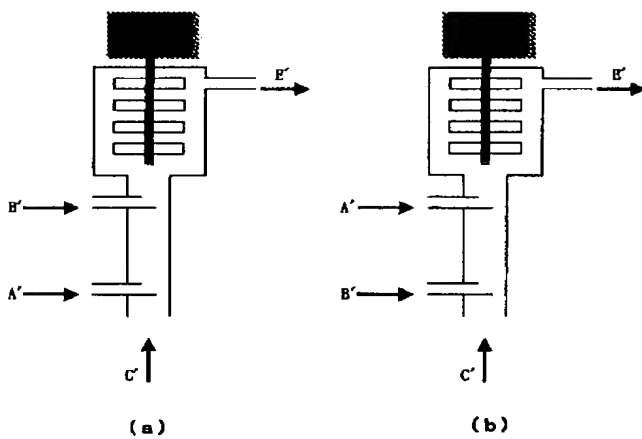
【Fig.3】



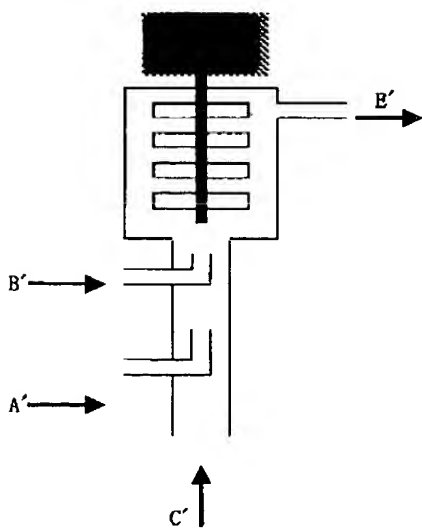
【Fig.4】



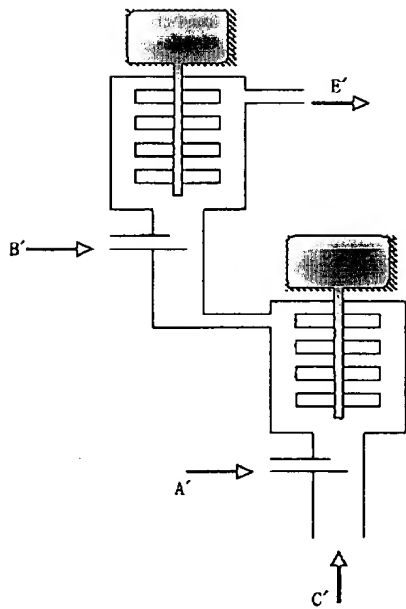
【Fig.5】



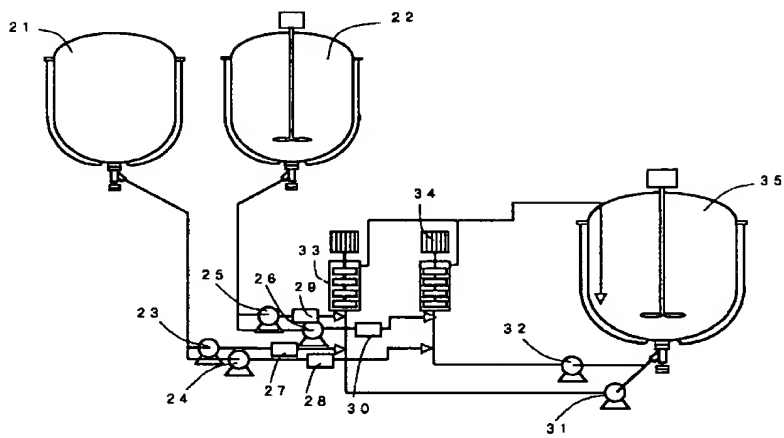
【Fig.6】



【Fig.7】



【Fig.8】



【Document Name】 Abstract

【Problems】 To provide a method for preparing a silver salt of an organic acid, which produces a thermally processed image recording material having high sensitivity and image stability after thermal development when the silver salt is used for the image recording material.

【Means for solving the problems】 A method for preparing a silver salt of an organic acid by reacting a solution containing silver ions and a solution containing an alkali metal salt of an organic acid, in which the reaction is performed in sealed mixing means and which comprises steps of supplying the silver ion-containing solution into a reaction field solution before introduced into the sealed mixing means, and supplying the solution containing the alkali metal salt of the organic acid into the reaction field solution or sealed mixing means.

【Selected figure】 None